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November 11, 2005

Mr. Tien Q. Duong  
5G-030, EE-32  
Forrestal Building  
U.S. Department of Energy  
Washington D.C. 20585

Dear Tien:

Here is the fourth-quarter FY 2005 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATTreports.html>.

Sincerely,

A handwritten signature in black ink, appearing to be "Venkat Srinivasan".

Venkat Srinivasan  
Manager  
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	E. Wall	DOE/OFCVT
	K. Abbott	DOE-BSO

LBID-2563 (4)

# **BATT TASK 1 CELL DEVELOPMENT**

## **TASK STATUS REPORT**

**PI, INSTITUTION:** V. Battaglia, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Cell Fabrication and Testing

**SYSTEMS:** Graphite/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (high-energy, high-voltage Li-ion), Graphite/LiFePO<sub>4</sub> (low-cost Li-ion), and Graphite/LiMn<sub>2</sub>O<sub>4</sub> (high-power Li-ion)

**BARRIERS:** Li-ion systems meeting performance, abuse, and life targets.

**OBJECTIVES:** The primary objective is to establish a test vehicle for the evaluation of new materials for high-power or high-energy, low-cost Li-ion cells.

**APPROACH:** The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of EVs, HEVs and FCEVs. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline cell chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects.

**STATUS OCT. 1, 2004:** Further benchmarking of the low-cost Li-ion baseline cell including high-temperature aging will be carried out with larger cell sets to demonstrate reproducibility. Diagnostic analysis of cell components from this study will be combined with those from previous cells to lend insight into the degradation mechanism occurring on the natural graphite electrode in the presence of LiFePO<sub>4</sub>.

**STATUS SEPT. 30, 2005:** Performance measurements on the candidate sources of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> will be carried out and compared to the baseline material from Seimi. Room-temperature benchmarking of this baseline chemistry will be completed. In addition, half-cell studies of LiMn<sub>2</sub>O<sub>4</sub> in LiBOB-containing electrolyte for the high-power baseline cell will be carried out. Pouch cells from HQ will be benchmarked with regard to performance and aging and distributed to the diagnostic projects for analysis. Electrodes and cells will be prepared and tested in support of modeling and synthesis projects for the various baseline systems.

**RELEVANT USABC GOALS:** Specific power 780 W/L, 15 year life, < 23% power fade.

### **MILESTONE:**

- |   |      |
|---|------|
| (a) Test 6 LiFePO <sub>4</sub> pouch cells from HQ  | 3/05 |
| (b) Benchmark LiMn <sub>2</sub> O <sub>4</sub> in LiBOB and LiPF <sub>6</sub> based electrolyte | 6/05 |

## PROGRESS TOWARD MILESTONES

### Progress toward Milestones

*Modifications to Milestones* - Since the AOP was written in July 2004, there have been some modifications to the expected progress and milestones. This was reported in the 1<sup>st</sup> Quarterly Report.

### Progress toward altered Milestones

(a) **Completed.** Results of this effort were reported in the 2<sup>nd</sup> Quarterly Report.

(b) **Suspended.** As stated in the Approach on the previous page, a primary responsibility of this group is to make good, repeatable cells. At the BATT Review on June 1, we presented results that demonstrated our ability to make repeatable cells with low impedance. Since the review (reported below) we have found that the cells we make reach the end of life criteria in four weeks. We believe the problem is that there is water in the cells. We do not know or understand the total affect that water plays on cell performance but we have been told that it even affects the physicochemical properties of SEI on the anode. We do not think it is proper to evaluate cell chemistries if there is water in the cells, and for this reason we have postponed the evaluation of  $\text{LiMn}_2\text{O}_4$  until our cell making capability has been upgraded.

### Progress beyond Milestones

Just before the June review, we made four cells from a single batch of slurry. The cells were measured to have an average ASI of  $32 \text{ ohm-cm}^2$  with a 4.1 % coefficient of variation. Subsequently, those cells were aged at  $45^\circ\text{C}$  for four weeks and reevaluated. It was found that the impedance of those cells increased to an average of  $38.5 \text{ ohm-cm}^2$  after the aging period. We believe we have a problem of water in the cells. To investigate this further, we built four more cells, but this time we encased two of those cells in glass. (Two cells were each placed between two sheets of glass and sealed with epoxy around the edges.) These cells were made from the same laminates cast to make the first batch of cells. The second batch of cells was characterized and found to have an average impedance of  $30.6 \text{ ohm-cm}^2$ . However, when these cells were aged their impedance increased to  $60 \text{ ohm-cm}^2$ . This was independent of whether they were encased in glass. These results suggest that water is getting into the cells during fabrication.

Since the review, we have been working with other cell making institutions to improve our cell fabrication capability. We visited Farasis in June, we visited Argonne in August, and we were visited by three members of the Hydro-Québec team in September. We also visited MSA and Yardney in September. Next month we will visit Quallion. The results of all of these visits have been to improve our cell pouch sealing methodology, and to better appreciate the precautions that need to be taken to prevent water from getting into cells during the fabrication process. To support this effort, we have ordered another glovebox (due to arrive at the end of November) and an advanced Karl Fischer machine with sample heating capability.

In the meantime, we have acquired SEM, BET, and PSD information on all twelve of the different battery materials that potentially could go into our cells. We have performed TEM for four investigators. We also have been working to set-up a ten year old ARC that recently arrived from a previously completed DOE program with SRI.

In addition, we have tested pouch cells from Hydro-Québec that indicate that they may also have problems with water in their cells. These cells lose capacity continuously with cycling. A new batch will arrive in early October. This will be the first batch sent to us since their visit.

## TASK STATUS REPORT

**PI, INSTITUTION:** T.J. Richardson, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

**SYSTEMS:** High-voltage, high-power: Gr/LiBOB+ $\gamma$ BL:EA/LiMn<sub>2</sub>O<sub>4</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>

**BARRIER:** Short lifetimes, poor abuse tolerance

**OBJECTIVES:** Support cell development and diagnostics tasks through structural characterization of active electrode components before, during, and after cycling. Protect cells against degradation and failure due to overcharging by means of lightweight, inexpensive protection mechanisms. Investigate particle isolation and oxygen loss mechanisms in composite electrodes. Synthesize and evaluate alternative electrode materials.

**APPROACH:** Address primary causes of power and capacity fading by correlating them with changes in the composition and structure of active materials and composite electrodes. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Continue to develop a reversible overcharge protection mechanism based on components that automatically short overcharged cells. Discover improved cell systems through a limited program of synthesis and evaluation.

**STATUS OCT. 1, 2004:** Composition and structural analyses of BATT Task 1.1 electrodes have contributed to our understanding of failure and degradation modes in the baseline systems. Electroactive conducting polymers capable of providing overcharge protection in Li-ion cells with cathode potentials above 4.0 V have been characterized. New cathode materials were synthesized and evaluated for introduction into BATT chemistries.

**STATUS SEPT. 30, 2005:** Improvements in chemistry, morphology and distribution of highly conducting polymers will permit protection of high-power cells against overcharging at rates as high as 3C. High-rate electrode materials will have been characterized for stability and compatibility with electrolytes.

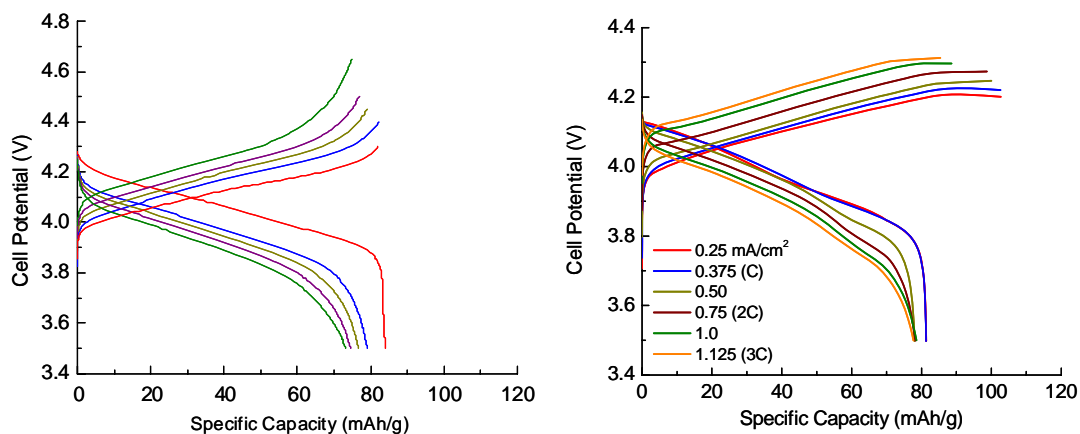
**RELEVANT USABC GOALS:** Abuse tolerance to cell overcharge and short circuit, 30 ohm-cm<sup>2</sup> area-specific impedance.

**MILESTONE:**

Protect LiMn<sub>2</sub>O<sub>4</sub> cells against 10 cycles of 5% overcharge at 3C or higher. (July 2005)

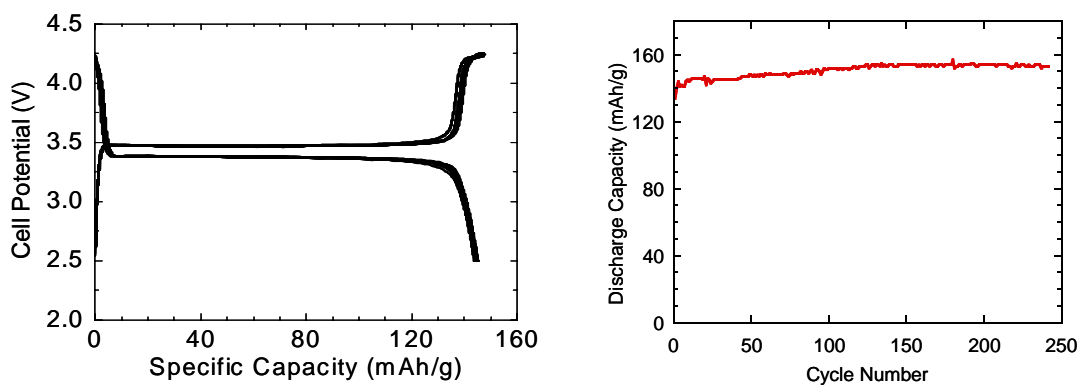
## PROGRESS TOWARD MILESTONE

High rate (up to 3C) overcharge protection using a bilayer conducting polymer composite separator was demonstrated in lithium cells with spinel-type  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  cathodes at different charge-discharge rates. Because the resistance across the polymer-impregnated separator varies with current density, the potential at which the cell is shorted increases with the charging rate (Fig. 1). Excellent capacity retention was observed even at the highest rate.



**Figure 1.** Variable rate charge-discharge curves for unprotected and protected  $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  cells.

The long-term stability of the conducting polymer-impregnated separator is shown by the stable discharge capacity of a  $\text{LiFePO}_4/\text{Li}$  cell that was overcharged by 5% on each cycle at a C/2 rate (Fig. 2). The polymer shunt maintained the cell potential below 4.3 V.



**Figure 2.** Discharge capacity of protected  $\text{LiFePO}_4/\text{Li}$  cell overcharged by 5% on each cycle.

## TASK STATUS REPORT

**PI, INSTITUTION:** K. Zaghib, Hydro-Québec (IREQ)

**TASK TITLE - PROJECT:** Cell Development - Lithium-Ion Polymer Batteries with Low-Cost Materials

**SYSTEMS:** Low-cost Li-ion

**BARRIER:** High cost of Li-ion batteries

**OBJECTIVES:** Fabricate Li-ion/polymer cells ( $4\text{ cm}^2$  area) using cell chemistries proposed by DOE, and send 50% of the total cells to LBNL for testing. Optimize gel formation as a function of the % plasticizer content; optimize the thermal cross-linked temperature by using new polymer with ionic liquid or liquid electrolyte as plasticizer. Determine the conductivity of gel electrolyte as a function of plasticizer content, particularly at low temperature. Study the interface of gel electrolyte in contact with the electrode active materials.

**APPROACH:** Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and to evaluate these materials in Li-ion/polymer cells. Additional work will focus on gel polymers, as well as studies to identify an appropriate salt and solvent to increase the performance and charge/discharge rate of Li cells at low temperatures. The gel electrolyte will be compared to a liquid electrolyte (100%) by measurements in half cells and Li-ion polymer cells at low temperatures.

**STATUS OCT. 1, 2004:** We will optimize the composition of anode (natural graphite, fibers) and cathode materials in the electrodes as a function of the water-soluble binder (WSB) (no fluoride), with the goal of reducing the amount of binder by 50% compared to standard electrodes with PVDF. To reduce the amount of binder and the cost of the coating, we will demonstrate a new coating process using WSB in the anode and cathode ( $\text{LiFePO}_4$ ). Also, we expect to show the effect the soluble WSB on other baselines chemistries ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ). A study of the effects of PVDF and WSB in electrodes to improve the safety aspect of the battery will be completed. We expect to provide primary cycling data (including PNGV protocol) from Li-ion/polymer cells containing WSB and a low-cost Li salt. We will continue to develop carbon-coated  $\text{LiFePO}_4$  (Phostech) with higher tap density.

**STATUS SEPT. 30, 2005:** We will determine the composition of gel electrolytes, which are based on a new high-viscosity polyether gel, as a function of the amount of ionic liquid (molten salt) or liquid electrolyte used as plasticizers. These plasticizers should be beneficial in reducing the amount of polymer and to increase the safety of the cell, and will be compared to results obtained with electrodes containing PVDF and WSB. We will optimize the gel electrolyte with different anodes based on hard carbon, soft carbon, and graphite to select a good candidate for low-temperature and high-rate applications. The amounts of cathode material and gel electrolyte will be optimized to increase the high-rate performance of  $\text{LiFePO}_4$ , and other baselines chemistries ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ). ARC safety tests using a new gel electrolyte in contact with anodes and cathodes will be evaluated in collaboration with J. Dahn, and details are under discussion. We expect to provide cycling data, including the PNGV protocol, in Li-ion polymer cells that contain gel electrolyte based on polymer-ionic liquid, polymer-liquid electrolyte, and 100% liquid electrolyte.

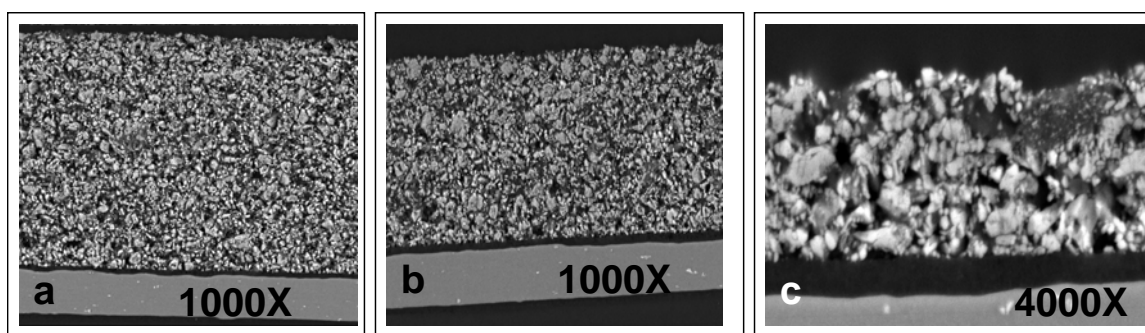
**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10-year life, < 20% capacity fade.

**MILESTONES:** 1) Identify an ionic liquid with low-cost, high-viscosity polymer (April 2005). 2) Deliver thirty (30) cells to LBNL (10 cell every four months). 3) Produce  $\text{LiFePO}_4$  with high tap density at Phostech. (February 2005).

## PROGRESS TOWARD MILESTONE

During this quarter we have focused our effort on optimizing our cells assembly protocol. Based on the LBNL recommendation on electrode dimension: ( $3 \times 4 \text{ cm}^2$ ) for cathode and ( $3.15 \times 4.15 \text{ cm}^2$ ) for the anode, two punches were fabricated for this purpose. The HQ technical team visited LBNL in September for discussions with the technical team on cell assembly and to develop a common assembly protocol.

The second goal was to address the water soluble binder (WSB). Coating with WSB was successfully realized with  $\text{LiFePO}_4$ , and different film thicknesses were coated. The benefits of using WSB were very large compared to PVDF cathode. The thickness can vary from  $75 \text{ }\mu\text{m}$  to very thin films of  $10 \text{ }\mu\text{m}$  (Fig. 1). At this level of thickness, we had difficulty in making films with PVDF, particularly at high capacity where the films tended to fold upward. The cathodes obtained with WSB are uniform and have good adhesion. The electrode density was  $2 \text{ g/cm}^3$  without lamination.



**Figure 1.** Water soluble binder cathode with different thickness; a)  $75 \text{ }\mu\text{m}$ , b)  $46 \text{ }\mu\text{m}$  and c)  $10 \text{ }\mu\text{m}$ .

Research was also conducted on the iron phosphate cathode material and its performance at  $60^\circ\text{C}$ . A Li-ion cell ( $\text{LiFePO}_4/\text{LiPF}_6\text{-ECDEC/graphite}$ ) was cycled at  $60^\circ\text{C}$ . After more than 200 cycles at C/1 rate both on charge and discharge, no capacity fade was observed. The EDX analysis did not show any trace of iron at the anode surface, indicating good thermal stability and no solubility of  $\text{LiFePO}_4$ .

Toward the third goal, we started optimizing a new polymer gel having less than 5% polymer. This new gel polymer will be validated with graphite and  $\text{LiFePO}_4$  anode and cathode material, respectively. The polymer electrolyte was first filled in the cell and then thermally cross-linked. The polymer formed an over-coated gel film on the polypropylene (PP) separator after being thermal cross-linked at  $60^\circ\text{C}$  for 1 h. Li-ion cells with this new gel polymer will be cycled and delivered to LBNL by December 2005.

For the last goal, we started characterisation of some ionic liquids. The first measurements were on the viscosity. The data shows that the viscosity decreases with increasing temperature.

Two abstracts were submitted for the ECS meeting at Los Angeles CA in October 2005:

1. “ $\text{LiFePO}_4$  and Graphite Anode Using Water Soluble Binder for Low-Cost Li Polymer Batteries,” K. Zaghib, P. Charest, A. Guerfi, M. Dontigny and M. Peticlec. Abstract # 216.
2. “ $\text{LiFePO}_4$ -Li-ion Polymer Technology For Cleaner Transportation,” K. Zaghib, V. Battaglia, P. Charest, V. Srinivasan, A. Guerfi and R. Kostecki, Abstract # 848.

## TASK STATUS REPORT

**PI, INSTITUTION:** D. Wheeler and J. Harb, Brigham Young University

**TASK TITLE – PROJECT:** Design, Optimization, and Fabrication of Li-ion Electrodes for High Power Applications

**SYSTEM:** Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>

**BARRIERS:** Electrode impedance that limits power density and cycle life

**OBJECTIVES:** Improve battery power and life through novel electrode structures. Increase understanding of how electrode morphology influences performance. Develop tools to analyze high-rate performance of electrolytes.

**APPROACH:** We will explore methods for maximizing the high-power performance of low-cost LiFePO<sub>4</sub> composite cathodes. Our efforts will include the use of a variety of electronically conductive additives in order to improve high-rate performance and diminish capacity fade due to loss of conductivity/connectivity. Electrode structure will also be optimized to enhance performance. In addition, as part of our efforts to optimize electronic and ionic conduction in composite electrodes, we will conduct Hall-effect experiments and molecular dynamics (MD) simulations in order to determine transport properties for liquid electrolytes.

**STATUS OCT. 1, 2004:** This will be our first month of the new project. We will acquire the materials required to begin fabrication and testing of LiFePO<sub>4</sub> cathodes. Initial efforts will also include work on the construction of an apparatus for Hall-effect experiments. An improved set of *ab initio* based potentials for MD simulations will be developed.

**STATUS SEPT. 30, 2005:** We will have demonstrated the power and cycle-life improvements possible with different types of electronically conductive additives in LiFePO<sub>4</sub> cathodes, and identified the factors that limit performance. Processing steps for the mixing and application of improved cathode slurries will also have been demonstrated. We will have shown proof-of-concept results for obtaining the electrolyte transference number using the Hall Effect. MD simulations of the transport properties of LiPF<sub>6</sub> in liquid carbonate electrolytes, as a function of temperature and concentration, will be completed.

**RELEVANT USABC GOALS:** HEV-related goals of 30  $\Omega\text{-cm}^2$  impedance and 300k cycles

### MILESTONES:

- (a) Demonstrate that Hall Effect can be used to measure transference numbers. (Apr. 2005)
- (b) Complete initial investigation toward optimizing LiFePO<sub>4</sub> cathode. (Aug. 2005)



## PROGRESS TOWARD MILESTONES

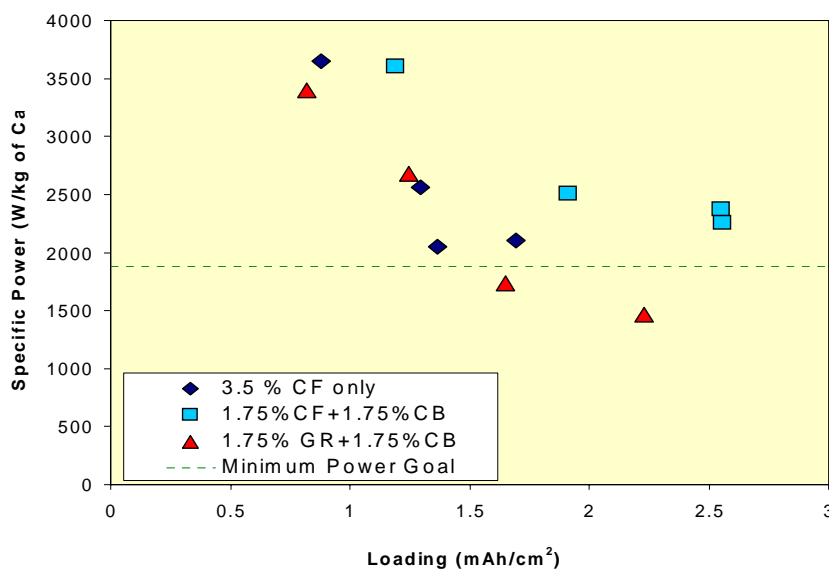
Efforts in the past quarter included additional fabrication and testing of  $\text{LiFePO}_4$  cathodes containing new combinations of conductive carbons, in particular carbon fibers. The ongoing development of experimental and computer-simulation techniques to investigate liquid electrolyte transport properties was also continued this quarter under BATT funding. These investigations will better enable us to overcome the bottlenecks to high-power-density and inexpensive Li rechargeable batteries.

As highlighted here, we fabricated and tested cells utilizing carbon-coated  $\text{LiFePO}_4$  active material and carbon-coated current collector (both supplied by Hydro-Québec) in the cathode and having a Li counter electrode. The cathode slurries contained a total of 3.5% (by weight) carbon additives to promote electronic conductivity. The three additives used were graphite (GR), carbon black (CB), and carbon fiber (CF). The vapor-grown carbon fibers, obtained from Pyrograf Products, have diameters in the range 70-200 nm and lengths in the range 50-100  $\mu\text{m}$ .

Prior work in our group has shown that the cells we fabricate get reasonable capacity values over a range of discharge rates. Shown in Fig. 1 are recent results from 10-s pulse-discharge tests at 50% depth of discharge. Each point is the maximum power achieved for the half cell within voltage constraints (minimum 2.2 V). Also shown on the plot is the USABC discharge power goal for HEV applications. The goal has been converted to a cathode-weight basis by assuming the cathode is one-third of the total battery weight. Not shown are similar results for HEV pulse-charging tests.

The pulse tests show that  $\text{LiFePO}_4$  cathodes can meet the HEV goals over a range of loadings, with the optimal loading at around 1  $\text{mAh}/\text{cm}^2$  for the three carbon compositions. At higher loadings the cells containing carbon fibers plus carbon black performed best. Higher loadings are desirable in order to increase energy density of the cells.

Finally, we note that our prototype Hall-effect test system for obtaining ion transference numbers was recently completed. Validation tests using electrolytes with known transference numbers will be carried out in the first quarter of FY 2006.



**Figure 1.** Maximum discharge-pulse specific power (cathode weight basis) as a function of cathode loading and carbon composition.

## BATT TASK 2 ANODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Anodes - Non-Carbonaceous Materials

**SYSTEMS:** Graphite/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Graphite/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Cost, low temperature and abuse tolerance limitations of Li-ion batteries

**OBJECTIVES:** To replace graphite with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project addresses the need to improve irreversible capacity losses of intermetallic electrodes as well as the low-temperature operation and abuse tolerance of Li-ion cells.

**APPROACH:** Our approach over the past few years has been to search for inexpensive intermetallic electrodes (primarily for EV applications) that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and a capacity of 300 mAh/g and ~2000 mAh/ml. We will focus on: 1) matrix reactions that, when combined with insertion reactions, may have a stronger chance of success than when topotactic reactions are used alone; 2) composite electrodes with Al, Si, Sn, and Sb components to determine their rate capability; 3) pre-lithiation reactions to fabricate charged electrodes for use against non-lithiated metal oxide electrodes and to overcome first-cycle irreversible capacity loss; 4) low-potential metal oxide negative electrodes coupled with the high-potential layered and spinel cathodes of Task 4.1 to yield high-rate and abuse-tolerant Li-ion cells (>3 V) for HEV applications.

**STATUS OCT. 1, 2004:** Composite electrodes containing graphite and a metal component such as Sn or Sb delivered the targeted capacity milestone of 300 mAh/g for 100 cycles. Although in some instances an irreversible capacity loss <20% was achieved on the first cycle, this capacity loss was still a limiting parameter in most cells. Efforts to find a high-performance, low-potential (<1 V vs. Li<sup>0</sup>) metal oxide anode were unsuccessful. Several Li<sub>1+y</sub>MX<sub>2</sub> reactions (*e.g.*, M=V, Mn, Ni, Co) were modeled by *ab initio* calculations; theoretical predictions were verified by experimental observations. Studies of SEI layers on intermetallic electrodes were in progress.

**STATUS SEPT. 30, 2005:** The low-temperature behavior and rate capability of carbon/metal (intermetallic) electrodes will have been determined. The first-cycle irreversible capacity loss of the electrodes and their capacity retention upon cycling will have been improved.

**RELEVANT USABC GOALS:** 10 year life, <20% fade over a 10-year period.

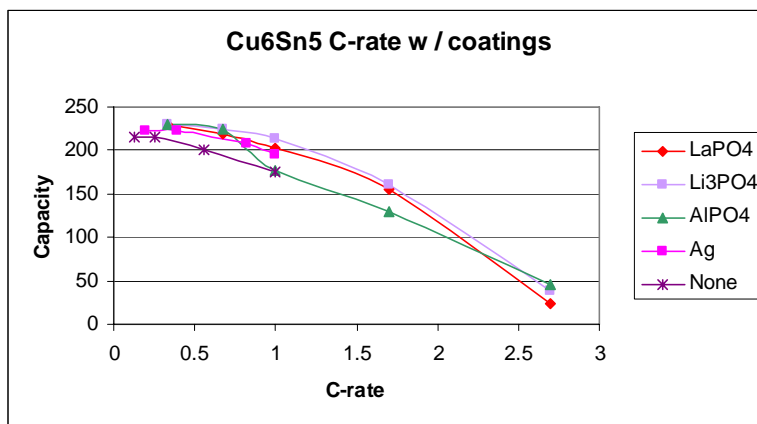
**MILESTONES:** By September 2005: 1) Carbon/intermetallic electrodes: 5-15% irreversible capacity fade on initial cycle; 300 mAh/g for more than 100 cycles; low-temperature rate capability determined. 2) Prelithiated carbon/intermetallic/metal oxide electrodes: synthesized and evaluated electrochemically; 3) Metal oxide electrodes: electrochemical evaluation against high-potential layered and spinel electrodes in >3 V Li-ion cells.

## PROGRESS TOWARD MILESTONES

We have investigated (1) the utility of FMC's stabilized Li metal powder product 'Lectro Max' for pre-reducing main group metal oxides, (2) the effect of surface coatings on the rate capability of  $\text{Cu}_6\text{Sn}_5$ .

'Lectro Max' is a powdered form of Li metal with a thin coating of lithium carbonate. The coating significantly increases the air stability of the powder allowing it to be used in a lamination process. In our previous studies, we examined the ability of 'Lectro Max' to pre-lithiate, *ex situ*, a variety of metal oxide- and intermetallic alloy electrode materials prior to assembly in electrochemical cells through the use of uniaxial pressure. We showed that without activation (*i.e.*, reaction initiation), the Li metal typically formed a coating on systems requiring metal displacement, *e.g.*, metal oxides and intermetallics, and it tended to have some reductive effect on metal oxide insertion compounds. In our present study, we investigated various ways to activate the Li powder, *ex situ*, notably by calendaring, mild heating in the presence of electrolyte, and ball milling. With tin oxides we found that (1) uniaxial pressure and calendaring tended to activate the Li metal on the surface but it reacted minimally with the underlying material, (2) mild heating in the presence of electrolyte had no effect, and (3) ball milling fully reduced tin oxides to a mixture of tin and lithia. Work continues on the effect of ball milling 'Lectro Max' with intermetallic- and metal-oxide insertion electrode materials.

We are continuing our studies on the effect of surface coatings on the rate capability of intermetallic anodes. At the BATT Review in May, we reported on how silver enhanced both the room temperature and low temperature (0 °C, -30 °C) rate capability of  $\text{Cu}_6\text{Sn}_5$ . We have extended these studies to phosphate coatings that might help passivate highly lithiated metal surfaces. Coatings were deposited by a solution precipitation method and dried under vacuum at 120 °C. Early results, as presented in Fig. 1, indicate that the coatings enhance the room temperature rate capability of  $\text{Cu}_6\text{Sn}_5$  by an amount similar to silver-coated electrodes, the best result being obtained from a 5 wt%  $\text{Li}_3\text{PO}_4$ -coated sample. The exact reasons for the enhanced capacities delivered by the phosphate-coated electrodes at the lower rates are not yet understood.



**Figure 1.** Variation of capacity of coated  $\text{Cu}_6\text{Sn}_5$  electrodes as a function of rate

In the coming quarter, we plan to study the effect of electrolyte additives on  $\text{Cu}_6\text{Sn}_5$  anodes, to extend our low temperature rate studies to full cells and to initiate work on cobalt-substituted intermetallic materials.

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Anodes - Novel Materials

**SYSTEMS:** Li-Ion: all systems

**BARRIER:** Cost, safety and volumetric capacity limitations of Li-ion batteries

**OBJECTIVES:** To replace the presently used carbon anodes with safer materials that will be compatible with low-cost manganese oxide and phosphate cathodes and the associated electrolyte.

**APPROACH:** Our anode approach is to explore, synthesize, characterize and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites, and on intercalating oxides. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

**STATUS OCT. 1, 2004:** We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al foil and expanded metal were found to have high capacities and react readily with Li, but its capacities faded rapidly upon cycling in carbonate-based electrolytes; Al-based alloys show behavior inferior to pure Al. Tin-containing materials, such as  $\text{MnSn}_2$ , cycle well for a few cycles before capacity fade sets in. Pure tin-foil anodes cycle better than pure Al or  $\text{MnSn}_2$ , but the cell impedance was found to increase markedly after about ten cycles; an expanded tin grid was marginally superior, but not sufficient to justify further study.

**STATUS SEPT. 30, 2005:** From our program to understand capacity fade of tin upon cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, and as a result to have identified several additional non-Al binary alloys; and to have improved the electrochemical performance of the materials identified.

**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit.

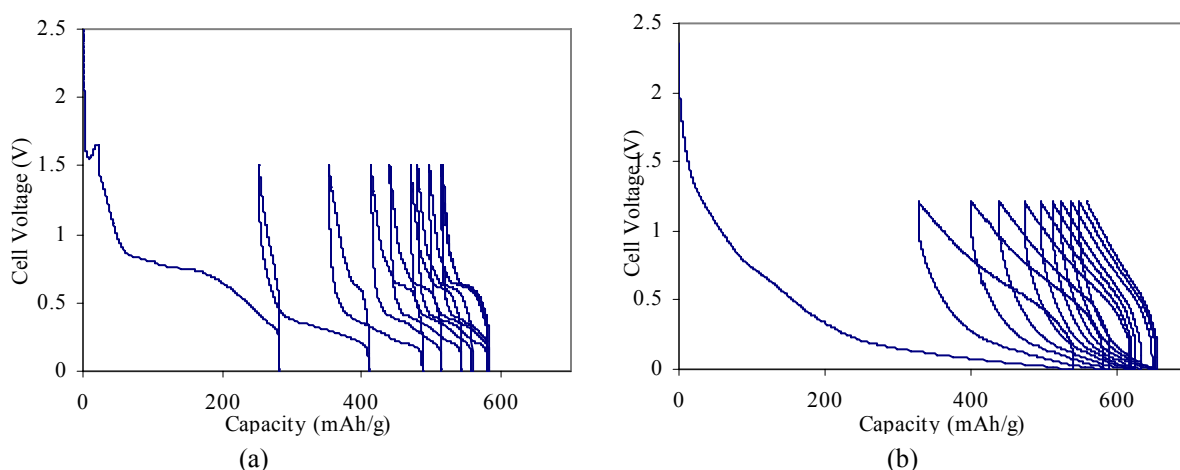
**MILESTONES:** (a) We will design a program to identify, understand, and mitigate the capacity loss upon cycling of simple alloy systems. This will result in a milestone to understand and define the key parameters determining capacity fade in pure tin and its alloys by June 2005, and to propose a means of remediating that fade. (b) We will identify the impact of electrolyte solvent and salt on the capacity retention and rate capability of pure tin, including first-cycle capacity loss, by October 2005.

## PROGRESS TOWARD MILESTONES

In previous reports we reported the electrochemistry of tin foil and expanded tin grids, and showed that they had higher capacities than graphite as the host for lithium. However, the capacity rapidly decays after 10 to 15 cycles to values comparable to that of graphite. Earlier we discussed the cycling of the  $\text{Sn}_2\text{Mn}$  phase, which showed initially a high capacity that fell off just as for tin itself.

This quarter we have initiated a study of the impact of replacing the manganese by cobalt to give mixed tin-cobalt phases such as  $\text{Sn}_2\text{Co}$ . We used two different samples, one made in-house by annealing the elemental powder under inert atmosphere (helium), and one commercially available sample. X-ray analysis showed that the former was predominantly  $\text{Sn}_2\text{Co}$  with some metallic tin and tin oxide contaminant. The latter was found to be essentially amorphous, with no obvious crystalline phases; electron microprobe analysis indicated a tin to cobalt ratio consistent with the composition  $\text{Sn}_2\text{Co}$  plus a little titanium, the carbon content was low if any was present.

The electrochemical behavior of these two samples is compared in Fig. 1. The as-synthesized sample gave poor behavior due to the existence of impurities. On the other hand the commercial sample shows an initial capacity of 550 mAh/g, which is approaching the theoretical capacity of around 610 mAh/g if all the tin reacts to give  $\text{Li}_{3.5}\text{Sn}$  as with tin foil. In both cases a significant fraction of the reacted Li could not be recovered on the charging cycle. The very different behavior of the two materials is now being investigated, as is the mechanical integrity of the electrodes on cycling; the smooth discharge curve of the commercial sample is typical of that expected for an amorphous material.



**Figure 1.** Cycling of  $\text{Sn}_2\text{Co}$ ; (a) in-house synthesized sample and (b) a commercial sample; both were cycled at a current density of  $1\text{mA}/\text{cm}^2$ .

**Further plans to meet or exceed milestones:** None

**Reason for changes from original milestones:** No changes

Publications and Presentations resulting from the work.

1. Quan Fan, Peter Y. Zavalij and M. Stanley Whittingham, "Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum," *Mater. Res. Soc. Proc.*, 835: K6.16 (2005).

## TASK STATUS REPORT

**PI, INSTITUTION:** A. West, Columbia University

**TASK TITLE – PROJECT:** An Investigation of the Stability of the Lithium Metal Interface

**SYSTEMS:** Li/Polymer/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>

**BARRIERS:** Interfacial instability (dendrite formation) during charge of Li metal anodes leads to limited cycle life

**OBJECTIVE:** Understand the influence of electrolyte composition, deposition rate, and applied potential on interfacial stability of Li in liquid and polymer electrolytes. Investigate the root causes (mechanisms) of dendrite formation.

**APPROACH:** Dendrite formation and growth will be monitored by electrochemical and optical methods as a function of electrolyte composition and applied potential. In an attempt to study the cause or causes of dendrite formation, the impact of pulse plating parameters on dendrite formation will be considered. Furthermore nucleation and growth of Li deposits will be characterized by electrochemical methods.

**STATUS OCT. 1, 2004:** New project initiated September 2005.

**STATUS SEPT. 30, 2005:** Will set-up laboratory and hire personnel to conduct the necessary experiments. Will establish experimental preliminary methodology for building lithium metal batteries.

**RELEVANT USABC GOALS:** Specific Energy = 200 Wh/kg and Specific Power = 400 W/kg;  
Energy Density = 300 Wh/l and Specific Power = 600 Wh/l; 1000 cycles

### MILESTONES:

1. Establish Columbia University experimental setup and evaluate methods of characterizing dendrite formation (April 2006).
2. Quantify the influence of electrolyte properties and deposition conditions on dendrite formation and growth (October 2006).

## **PROGRESS TOWARD MILESTONES**

This is a new project, commencing in September 2005. Based on discussions with and feedback from BATT Program investigators, we have established the preliminary methodology for building lithium metal batteries. We have purchased and set up a glove box (with the exception of a humidity sensor). Furthermore, an existing student, Owen Crowther, has been transitioned to this project.

Preliminary experiments have been only partially successful, as we continue to modify the design. We have had continued discussions with BATT program investigators for purposes of experimental design.

## TASK STATUS REPORT

**PI, INSTITUTION:** G.A. Nazri and D. Curtis, University of Michigan  
T. Malinski, Ohio University

**TASK TITLE - PROJECT:** Anodes – Novel Composite Anodes for Lithium-ion Batteries

**SYSTEMS:** Low-cost Li-ion battery, improved safety, long cycle and calendar life

**BARRIERS:** Poor cycle life, poor safety, self-discharge, and electrolyte decomposition

**OBJECTIVES:** Develop a low-cost and safe composite anode with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

**APPROACH:** Prepare alternative composite anodes *via* reactive mechano-milling of anode materials with lithium or lithium hydride to eliminate the inherent irreversible capacity loss of metal-oxide anodes. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide anodes in presence of electrolyte, and improve the kinetics of the Li insertion - extraction process by optimization of anode particle size to nanoscale.

**STATUS OCT. 1, 2004:** The optimization of mechano-milling process parameters for reactive reduction of metal oxide, nitride, and phosphides anodes will be completed. The chemical nature of the SEI formed on metals and alloys after due to reduction of their oxides, nitrides, and phosphides will be completed. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1 M LiPF<sub>6</sub>) will be studied.

**STATUS SEPT. 30, 2005:** Final report will be submitted.

**RELEVANT USABC GOALS:** Exceeding 10-year life, high power battery electrode, low cost battery and high safety

**MILESTONES:** Final report will be submitted by June 30, 2005.



## **PROGRESS TOWARD MILESTONES**

In this quarter, a final report of the activities conducted on using composite anodes in Li-ion batteries was submitted. With this submission, the milestone has been achieved and this project is deemed complete.

## **BATT TASK 3 ELECTROLYTES**

### **TASK STATUS REPORT**

**PI, INSTITUTION:** N.P. Balsara, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Development and Polymer Electrolytes and Gels for Advanced Lithium Batteries

**SYSTEMS:** Nanostructured polymer electrolytes based on polystyrene-polyethyleneoxide (PS-PEO) block copolymers. End crosslinked PEO swollen with EC:DEC mixtures.

**BARRIERS:** Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade.

**OBJECTIVES:**

- Obtain PS-PEO diblock copolymer films with maximum ionic conductivity.
- Study the stability of PS-PEO electrolytes against Li electrodes.
- Develop and characterize the properties of uniformly crosslinked PEO gels swollen with EC:DEC mixtures.

**APPROACH:** To synthesize and characterize new polymeric electrolytes. This includes gel electrolytes and nanostructured dry polymer electrolytes. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, rheology and light scattering to obtain new insights into the rate-limiting transport processes. The materials will be tested for stability against Li electrodes.

**STATUS OCT. 1, 2004:** Rheological properties of PEO/LiTFSI and polytetramethyleneoxide/LiTFSI (PTMO/LiTFSI) mixtures have been measured and analyzed. Polystyrene-polyethyleneoxide (PS-PEO) block copolymers will be synthesized. Low cost synthetic routes for uniformly crosslinked polymer gel electrolytes will be established. The relevant mechanical and electrical properties of the electrolytes will be measured.

**STATUS SEPT. 30, 2005:** Synthesis and characterization of a new class of gel electrolytes with uniform crosslinking density. Completion of structural and conductivity measurements on the gel electrolytes. Characterization of nanostructured PS-PEO electrolytes including tests of stability against Li electrodes. We will continue collaborating with John Kerr and other members of the BATT program on the thermodynamic and rheological characterization of polymer gel electrolytes.

**RELEVANT USABC GOALS:** 30 ohm-cm<sup>2</sup> area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit.

**MILESTONES:**

1. To measure conductivity, mechanical properties, and stability against Li electrodes of dry, nanostructured PS-PEO-based electrolytes. (Sept. 2005)
2. Synthesize and characterize uniformly crosslinked PEO systems for gel polymer electrolytes applications. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

### 1. Nanostructured Polymer Electrolytes.

We continued work on electrical measurements of our polystyrene-b-polyethyleneoxide diblock copolymers. We made measurements on 1 mm thick and 7.5 mm diameter samples with a salt concentration of EO/Li = 50. The temperature was varied from 60 to 120°C in 10°C increments. Our results indicate that we are able to achieve conductivities in the range of the theoretical upper limit expected from samples with an ethylene oxide volume fraction of 0.38. This was achieved despite no special processing steps to align the PEO channels. We made several samples to establish the reproducibility of our data and results indicate that the conductivity values are repeatable. Also, we made samples with varying salt concentrations – with EO/Li ratio of 10, 15, and 20 in addition to our samples with EO/Li ratio of 50 with the temperature again varied from 60 to 120°C in 10°C increments. Conductivity results from these experiments follow the expected trend of increasing conductivity with increasing salt content and it was also found that the same correlation with expected theoretical results were observed. Furthermore, we observed a maximum conductivity at an EO/Li of ~15 for all the salt concentrations studied. This trend has been observed with other polyethyleneoxide systems and is attributed to the balance of the number of charge carriers with decreased mobility resulting from the formation of ion pairs.

Sets of experiments were also conducted to investigate the effect of film thickness on the conductivity of our polymer electrolytes. These samples were made by pressing the freeze-dried polymer samples within Teflon spacers with a mechanical press at a temperature of 80°C. A delicate balance between the applied pressure and temperature was critical as too much pressure could lead to the cracking of the thin samples, while high temperature could result in the sample deformation. The varying thicknesses include 1.0mm, 0.75mm, 0.50mm, 0.30mm, 0.20mm, and 0.10mm. Initial results are encouraging as we observe that our conductivity values are independent of the thickness; however, more experiments will be conducted to reproduce and confirm our results.

Transmission Electron Microscopy (TEM) and Small-Angle X-ray Scattering (SAXS) were made to confirm sample morphology. Both techniques indicate a perforated lamellae structure with weak long-range order. The peaks from SAXS were observed at  $\sqrt{4}$  and  $\sqrt{7}$ , the characteristic peaks for the hexagonally-perforated lamellae phase.

We have begun experiments with non-blocking Li electrodes using both DC and AC voltages. Our aim is to observe conductivity throughout the bulk of the film sample with Li electrodes. These experiments are crucial as we can learn more about the stability of our cells and its performance in actual battery systems.

## TASK STATUS REPORT

**PI, INSTITUTION:** J. Kerr, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes - R&D for Advanced Lithium Batteries

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>  
High-voltage, high-power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIERS:** Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade, low abuse tolerance.

### OBJECTIVES:

- Determine and quantify the improvement (if any) in abuse tolerance of polymer gel electrolytes over liquid electrolytes.
- Determine the limitations on Li-ion transport in polymer gel electrolytes and the electrolyte component of composite electrodes and develop materials capable of high-power operation at ambient temperature with lithiated carbons/Li metal alloy anodes and high-voltage cathode materials.
- Determine the feasibility of the use of Li metal electrodes with polymer gel electrolytes and provide operating conditions that prevent dendrite growth and high coulombic efficiencies at HEV rates.

**APPROACH:** A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

**STATUS OCT. 1, 2004:** Characterization of mechanical, transport, electrochemical, and chemical properties of cross-linked comb-branch and linear polymers and polyelectrolytes will be completed for both dry polymer electrolyte used with Li metal and polymer gel electrolytes with carbon. Modifications of Li metal surfaces and conducting carbon particles will be assessed.

**STATUS SEPT. 30, 2005:** State-of-the-art polymers will be procured or synthesized to prepare polymer gel electrolytes with the base system electrolyte components. The effects of the gel on abuse tolerance and transport properties will be determined. The performance of single-ion conductor gels will be compared with the binary systems. Compatibility of the polymer electrolyte and polyelectrolyte gels with Li metal and Li alloy electrodes will also be explored.

**RELEVANT USABC GOALS:** 15 year life, <23% power fade, specific power 625 W/kg at the system level.

### MILESTONES:

- 1) Demonstrate and quantify the change in abuse tolerance resulting from use of gel polymer electrolytes relative to liquid electrolytes in the three cell systems. (Sept. 2005)
- 2) Quantify the effect of gel polymer electrolytes on transport properties relative to liquid electrolytes. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

### 1. Abuse Tolerance of Gel Electrolytes.

DSC and TGA measurements on base line electrolytes have been carried out on the neat solvent components and the electrolytes containing the Li salts. Thermal treatment of electrolytes up to 85°C has shown that the LiPF<sub>6</sub> systems are more reactive than the LiBOB systems. Sampling of the electrolytes over time and analysis by GC and GPC shows the disappearance of the ring compounds (EC, γBL) and the appearance of products resulting from ring opening (DEOHCD) and PF<sub>5</sub> PF<sub>3</sub>=O as well as other unidentified but higher M.Wt. materials. Addition of gelling materials such as PEGDME250, 500 and 1000 alters the reaction pathways in the presence of LiPF<sub>6</sub>. It is apparent that the PEG materials are attacked by species formed from the LiPF<sub>6</sub> such as PF<sub>5</sub>. No reaction on the PEG components is observed if the salt is absent or exchanged for LiTFSI. The reaction of PF<sub>5</sub> with ethers is well known in the literature and leads to the formation of organic and inorganic phosphates as well as PF<sub>3</sub>=O. It is apparent that PEO-type polymers are incompatible with Li ion battery electrolytes for gelling purposes.

Since PF<sub>3</sub>=O is observed amongst the products and is also the product of reaction of PF<sub>5</sub> with water, accurate measurements of water content in the electrolyte are required. To this end, we have obtained a Mettler-Toledo DL390 Karl-Fischer Titrator equipped with a solids oven to carry out accurate measurements of water content in both electrolytes and solid cell components. Since the carbonate solvents used in Li-ion batteries are complicated in their reactivity we are working closely with the instrument manufacturer who has developed methods in collaboration with electrolyte manufacturers.

### 2. Transport Properties.

Transport property measurements of LiPF<sub>6</sub>-based gel electrolytes are difficult to carry out due to the reactivity issue. Salt diffusion measurements are particularly difficult due to the rapid growth of the interfacial impedance at Li electrodes. Experiments with lithiated graphite electrodes are under way to avoid this problem. However, the observation of large impedances at Li metal indicates that testing electrode materials against Li metal electrodes under high rate conditions is unwise.

Conductivity measurements of gel electrolytes against stainless steel electrodes show that the polymer additives such as PEO-type polymers that form fully swollen gels have significantly poorer transport properties than liquid electrolytes. The behavior of phase separating materials such as PVDF is considerably better. Further experimentation is under way to investigate further the effect of phase separation on both transport and interfacial properties. To assist in this investigation we have obtained a dynamic mechanical analyzer that is able to measure the properties of the polymers under immersed conditions. These measurements allow the extent of phase separation to be estimated.

## TASK STATUS REPORT

**PI, INSTITUTION:** S.A. Khan, P.S. Fedkiw, North Carolina State University;  
G.L. Baker, Michigan State University

**TASK TITLE - PROJECT:** Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

**SYSTEMS:** Low-cost composite polymer/gel electrolytes

**BARRIER:** Short lithium battery lifetimes and high costs.

**OBJECTIVES:** The ultimate objectives are to develop composite polymer/gel electrolytes that are low cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

**APPROACH:** Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 4-V cathodes.

**STATUS OCT. 1, 2004:** We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit desirable mechanical properties characteristic of solid electrolytes (*e.g.*, elastic modulus  $G' > 10^5$  Pa), yet have the processability of liquids and display conductivities rivaling liquid electrolytes ( $\approx 10^{-3}$  S/cm at 25°C). Fumed silica stabilizes the Li/electrolyte interface, effectively suppresses Li dendrite growth, and attenuates Al corrosion in presence of LiTFSI. We have found that addition of fumed silicas into low-MW PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V<sub>6</sub>O<sub>13</sub> cells. We have further determined that adding fumed silica improves the rheological properties of both high-MW and mixed-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. In this regard, adding fumed silica also improves the interfacial stability of the Li/electrolyte (both high-MW and mixed-MW PEO) interface and cycle performance of Li/V<sub>6</sub>O<sub>13</sub> cells. We have also synthesized single-ion conducting fumed silica [Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), R711-pLiAMPS.]

**STATUS SEPT. 30, 2005:** We expand the scope of our work to explore effects of adding fumed silica into BATT baseline electrolytes for Li-ion systems including rheological and transport properties, and interfacial stabilities. We will also examine Li/electrolyte interfacial stability and rheology of electrolytes consisting of mixtures of Li salt + single-ion conducting fumed silicas as a function of electrolyte composition and salt type.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade.

**MILESTONES:** (a) Investigate effects of adding fumed silica into BATT baseline electrolytes on transport and rheological properties, and interfacial stabilities, with a focus on low-temperature performance. September 2005.

(b) Examine the interfacial stability and rheology of mixtures of Li salt + single-ion conducting fumed silicas in polymer gel solvents as a function of silica concentration and salt type, including new lithium imide salts developed by Drs. DesMarteau and Creager at Clemson. September 2005.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

We focused our research on BATT baseline liquid electrolytes: lithium bis(oxalato)borate (LiBOB)/ $\gamma$ -butyrolactone (GBL): ethyl acetate (EA): ethylene carbonate (EC). We investigated conductivity as a function of LiBOB concentration in GBL + EA + EC mixtures at 0 and 60°C for different compositions of GBL+ EA + EC of 1:1:0, 1:1:0.1, 1:1:0.5, and 1:1:1 (wt). Conductivity has a maximum in salt concentration for all solvent compositions at 0°C; however, at 60°C for the GBL+EA+EC composition of 1:1:1, the conductivity monotonically increases with salt concentration up to 1.2 M. The salt concentration of maximum conductivity varies with temperature; for example, at 0°C it is around 0.7 M and at 60°C it is around 0.7-1.2 M, depending on the solvent composition. The molar conductivity monotonically decreases with salt concentration for all investigated solvent composition of GBL+EA+EC. The viscosity of GBL+EA+EC solvents at 1:1:0.1 as a function of LiBOB concentration at 5 and 25°C was investigated and the viscosity increases with salt concentration and decreasing temperature. The effect of EC content on electrolyte conductivity and viscosity was also investigated. At 0°C the conductivity decreases with increase in EC content; however, at 60°C the conductivity reaches a maximum with EC content at 1:1:0.1 (GBL:EA:EC). This behavior was common for all LiBOB concentrations studied. The viscosity of the electrolyte at fixed salt concentration of 0.7 M LiBOB increases with increasing EC content.

We continue to investigate liquid electrolyte and corresponding composite gel electrolytes for BATT baseline cells. The liquid electrolyte is 1M lithium bis(perfluoroethanesulfonyl)imide (LiBETI)/ EC:propylene carbonate (PC):dimethyl carbonate (DMC):diethyl carbonate (DEC) (1:1:1:1). Gel electrolytes were comprised of 10 wt% fumed silica + 1M LiBETI/ EC:PC:DMC:DEC (1:1:1:1) using two types of fumed silica: A200 (hydrophilic) and R805 (hydrophobic). Fumed silica has negligible effect on conductivity, and the conductivity is greater than 1mS/cm at 0°C. The addition of fumed silica significantly improves the rheological properties with elastic modulus above  $10^4$  Pa at 10 wt% fumed silica. Silica surface groups have significant effects on the rheology: a nonpolar surface (R805) forms a stronger gel than a polar surface (A200) because there is mismatch in solubility between silica surface and bulk medium. The gel rheological properties are similar for 25 and 5°C since the fumed silica dictates the mechanical stability. We conducted cycling of Li(Ni)/electrolyte/Li cells using 1M LiPF<sub>6</sub>, 1M LiBETI, and 10% R805 + 1M LiBETI, all in EC:PC:DMC:DEC (1:1:1:1) at room (23°C) and low (3~5°C) temperatures. Fumed silica improves the columbic efficiency and interfacial stability, and LiBETI salt has higher columbic efficiency than LiPF<sub>6</sub> salt. The columbic efficiency at low temperature is higher than that at room temperature for all investigated electrolytes. The columbic efficiency is in the following order: 10% R805 LiBETI gel > LiBETI liquid > LiPF<sub>6</sub> liquid.

- **Reason for changes from original milestone:** N/A

## TASK STATUS REPORT

**PIs, INSTITUTION:** D. DesMarteau and S. Creager, Clemson University

**TASK TITLE – PROJECT:** Electrolytes - New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

**SYSTEMS:** Graphite / LiPF<sub>6</sub>+EC:DEC / LiFePO<sub>4</sub>

**BARRIERS:** Poor electrolyte transport, low power, short life, abuse tolerance.

**OBJECTIVES:** (1) Synthesize new lithium fluorosulfonate and fluorosulfonimide salts for which anion attachment to a suitable plasticizer, scaffold, or matrix can be accomplished; (2) Characterize battery electrolytes made from the target salts with respect to structure, transport properties (conductivity, salt diffusion, transference), reactivity (*e.g.*, with electrode materials and current collectors), and battery performance (power, fade, interface stability).

**APPROACH:** Salts will be synthesized using variants of methods developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). Transport properties will be measured using EIS combined with restricted diffusion and potentiostatic and galvanostatic polarization techniques as needed. Reactivity with electrode materials will be studied by calorimetry, and half-cell and full-cell cycle testing will be performed using standard techniques with assistance from and/or in collaboration with other BATT researchers.

**STATUS Oct. 1, 2004:** Oligomeric salts of structure CF<sub>3</sub>SO<sub>2</sub>[N(Li)-SO<sub>2</sub>R<sub>f</sub>SO<sub>2</sub>]<sub>n</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> were provided to BATT coworkers for half-cell, rheology, and Al corrosion testing. Allyl ether salts of structure CH<sub>2</sub>=CHCH<sub>2</sub>O-CF<sub>2</sub>CFH-OCF<sub>2</sub>CF<sub>2</sub>-salt where salt=SO<sub>3</sub>(Li) and SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> were provided to BATT coworker Kerr for use making single-ion conductors. Transport studies on SPEs prepared using oligomeric fluorosulfonimide salts will be completed. Ionic melts of structure PEG-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt will have been synthesized and preliminary characterization including conductivity studies completed.

**STATUS SEPT. 30, 2005:** Plasticized electrolytes of general structure (X)-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt where salt = SO<sub>3</sub>Li or SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> and X = PEG, polyether, polysiloxane, and silica will have been synthesized and characterized with respect to conductivity and reactivity, and samples provided to other BATT workers for further testing.

**RELEVANT FREEDOMCAR GOALS:** 15 year life, <23% power fade, specific power 625 W/kg at the system level.

### MILESTONES:

- (1) Synthesize new electrolytes of general structure X-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt where salt = SO<sub>3</sub>Li or SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> and X = a PEG oligomer, a comb-branch network polyether, an OH-functionalized siloxane polymer, or a functionalized fumed silica particle. May 05.
- (2) Characterize the resulting electrolytes with respect to structure, transport properties, reactivity with anode and cathode materials, and battery performance using EIS, scanning calorimetry, half-cell and full-cell cycle testing, and other techniques as needed. Sept 05.



## PROGRESS TOWARD MILESTONES:

Work has continued on the synthesis and characterization of Li-conducting ionic melts of general structure  $X\text{-OCF}_2\text{CFH-OCF}_2\text{CF}_2\text{-salt}$  where  $X$  = a PEG oligomer and salt =  $\text{SO}_3\text{Li}$  or  $\text{SO}_2\text{N(Li)SO}_2\text{CF}_3$ , which are targeted due to their anticipated favorable combination of high ionic conductivity and lack of salt concentration polarization under high-power conditions. Progress has been made in scaling up reactions from several hundred milligrams to several grams per reaction scale. High yields were achieved by using less solvent and smaller reaction vessels which allow for more efficient cooling. We now routinely prepare melts several grams at a time. We have also developed an improved characterization technique using LC-MS to assess melt purity. We confirmed that our ionic melts are at least 95% pure and contain no more than 5% unreacted PEG. This finding is important since unreacted PEG could serve as a solvating medium in which salt concentration polarization could occur, thereby offsetting the advantages of the ionic melt for high-power applications. We hope to improve this assay to detect less than 1% impurity. Continuing melt characterization will focus on viscosity measurements (to correlate conductivity with viscosity and facilitate comparison with modeling studies by BATT co-workers Smith and Borodin) and calorimetry measurements in collaboration with Battaglia at LBNL to assess prospects for abuse tolerance.

DC polarization studies are being pursued on melts with the aim of confirming that they do not undergo salt concentration polarization on passage of DC current. We have experienced problems using  $\text{Li|electrolyte|Li}$  cells in these experiments, therefore we will seek to perform experiments using less reactive electrodes to assess the true properties of the electrolyte. We are consulting with BATT co-worker Zaghib to obtain samples of lithium titanate which is well suited for such studies due to its low reactivity and wide voltage plateau for Li insertion / deinsertion. It is hoped that these studies will allow definitive assessment of salt concentration polarization in the ionic melts.

In other synthetic work, salts of structure  $\text{CF}_2=\text{CFO-CF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{-salt}$  where salt =  $\text{SO}_3\text{Li}$  or  $\text{SO}_2\text{N(Li)SO}_2\text{CF}_3$ , were synthesized. These salts utilize the sulfonyl fluoride trifluorovinyl ether monomer used to make Nafion ionomers so they have good potential for rapid commercialization. PEG attachment has been accomplished and conductivity measurements are in progress. Also, a salt of structure  $\text{CF}_2=\text{CFO-CF}_2\text{CF}_2\text{-SO}_2\text{N(Li)SO}_2\text{-CF}_2\text{CF}_2\text{O-CF}=\text{CF}_2$  was synthesized. This salt is desired because it can be bis-functionalized with shorter-chain PEG oligomers which modeling studies have shown exhibit faster chain dynamics and should show higher conductivities relative to melts with longer chains.

Finally, we recently secured funding from Clemson to acquire a dedicated battery tester for performing cycling tests on cells fabricated at Clemson using ionic melt electrolytes. A four-channel tester is being purchased with delivery expected in November 2005. Swage-style cells are being fabricated, and electrode materials will be supplied in laminate form by BATT coworkers at LBNL and will be identical to materials being used by other BATT groups. This approach will ensure internal consistency in testing. With this unit in place we will be able to perform simple cycle testing experiments to assess the chemical compatibility of our electrolytes with electrodes, and their possible utility in cells under high-rate charging and discharging conditions. Preparation of electrolyte mixtures with active electrode materials for subsequent calorimetric studies of electrolyte reactivity with electrodes to assess abuse tolerance limits will also be pursued.

## TASK STATUS REPORT

**PI, INSTITUTION:** G.D. Smith and O. Borodin, University of Utah

**TASK TITLE - PROJECT:** Electrolytes - Molecular Modeling of Solid Polymer Electrolytes, Single Ion Conductors and Gel Electrolytes

**SYSTEMS:** Low -cost Li-ion

**BARRIERS:** Poor cation transport properties of gel electrolytes at ambient temperatures. Poor transport through SEI layer and poor chemical stability of the SEI layer.

**OBJECTIVES:** Gain molecular level understanding of the cation transport mechanism in single-ion conductor gel electrolytes. Develop new single ion conductor gel electrolytes with improved ion transport and mechanical properties. Understand Li transport in the SEI layer at the SEI layer/electrolyte interface.

**APPROACH:** Perform virtual synthesis and detailed characterization of a number of single-ion conductor electrolytes. Vary the structure of the single-ion conductor and the fraction of the plasticizer (ethylene carbonate, or EC) in gel electrolytes in order to optimize the ion transport and mechanical properties of polymer electrolytes. Perform MD simulations of the SEI layer and SEI/electrolyte interface to predict structural properties and Li transport of these battery components.

**STATUS OCT. 1, 2004:** Molecular dynamics (MD) simulations have been carried out on a number of single-ion conductors based on polyether type comb-branched polymers with TFSI<sup>-</sup> anions attached to side chains and ionic liquids with the structure LiTFSI-EO<sub>n</sub>-TFSILi as a function of temperature. The length of side chains, the Li<sup>+</sup> cation concentration, and the concentration of EC will be varied in order to determine the structure with the best ion transport parameters. Temperature dependence of the transport properties of gel electrolytes will be investigated at one concentration of plasticizer.

**STATUS SEPT. 30, 2005:** A detailed study of the influence of comb-branched copolymer architecture and plasticizer concentration on structural and transport properties of single-ion conductor gel electrolytes as a function of temperature will be investigated for the following parameters: the length of side chains and their spacing, salt concentration, and amount of plasticizer. The structure of the alkyl carbonate component of the anode SEI layer will be predicted. Lithium transport in the SEI layer components and at the interface of the SEI with the gel electrolyte will be studied on the molecular level using MD simulations.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade

**MILESTONES:** 1) Complete investigation of the effect of the length of side chains, salt concentration and EC concentration on structural and transport properties of single-ion conductor gel electrolytes at three temperatures. (June 1, 2005)  
2) Finish investigation of the anode SEI layer structure, Li transport, and interface with the gel electrolytes. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

### Li<sup>+</sup> Transport through Interfacial Electrolyte

Investigation of the free energy barriers for Li<sup>+</sup> transport from liquid binary electrolytes, dry and gel single ion conductors toward the model interface has been completed. Free energy barrier for a Li<sup>+</sup> approaching the surface is the lowest for liquid EC/LiTFSI electrolytes and the highest for the dry single ion conductor of (trifluoromethansulfonyl) imide anion immobilized on the comb-branched polymer-host side chain. The same single ion conductor plasticized with EC yielded free energy barriers between liquid electrolytes and dry single ion conductors. Interestingly, low molecular weight plasticizer (EC) tended to be situated near the interface, whereas Li<sup>+</sup> cations were found primarily complexed by polyether segments.

### Li<sup>+</sup> Transport in Liquid Electrolytes

In order to confirm our previous observations that approximately half of the total Li<sup>+</sup> transport in EC/LiTFSI is due to structure diffusion with another half coming from diffusion with a Li<sup>+</sup> cation coordinated by EC, we have conducted two additional simulations in which we have decreased the Li<sup>+</sup>/TFSI<sup>-</sup> interactions and increased Li<sup>+</sup>/EC interactions in such a way that the EC molecules cannot dissociate from the Li<sup>+</sup> on the scale of tens of nanoseconds. These additional simulations demonstrated that the Li<sup>+</sup> self-diffusion coefficient in EC/LiTFSI that does not allow Li<sup>+</sup> motion by structure-diffusion is 55% lower than the Li<sup>+</sup> self-diffusion coefficient in electrolytes with all original (“realistic”) interactions turned on that allows Li<sup>+</sup> diffusion by both mechanisms: vehicular diffusion with the Li<sup>+</sup> coordination shell and structure-diffusion. In contrast to the EC/LiTFSI solutions, Li<sup>+</sup> diffusion in pentaglyme was found to occur only by vehicular mechanism, indicating that in pentaglyme/LiTFSI lithium cations drag solvent molecules with them a significant distance.

### Li<sup>+</sup> Transport in Ionic Liquids and Plasticized Ionic Liquids

Over the last quarter we continued molecular dynamics (MD) simulations of a number of ionic liquids with the structure Li<sup>+</sup>/TFSI<sup>-</sup>(EO)<sub>12</sub> with TFSI<sup>-</sup> anion attached to oligoether backbone without a plasticizer and with 50 mol% plasticizer. Our simulations predicted that addition of plasticizer dramatically changed activation energy for the Li<sup>+</sup> diffusion in agreement with recent observations by Clemson group. Analysis of simulations indicated that Li<sup>+</sup> transport in unplasticized Li<sup>+</sup>/TFSI<sup>-</sup>(EO)<sub>12</sub> occurs by interchain hopping, whereas Li<sup>+</sup> transport in the plasticized ionic liquid is dominated by vehicular mechanism.

Inspired by a significant structure-diffusion contribution to Li<sup>+</sup> transport in liquid carbonate-based electrolytes, a number of novel structures comprised from carbonates tethered to a polymer backbone have been investigated in a hope to design novel single ion conductors with improved transport. Preliminary simulations indicated that Li<sup>+</sup> conductivities in these electrolytes exceeding dry single ion conductors based on (trifluoromethansulfonyl) imide anion immobilized on the comb-branched PEO-based comb-branched polymers.

**Reasons for Changes from Original Milestones:** N/A

## BATT TASK 4 CATHODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Cathodes - Novel Materials

**SYSTEMS:** High-voltage, high energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
High-voltage, high power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Cost and abuse tolerance of Li-ion batteries

**OBJECTIVE:** To develop low cost, high-energy and high-power Mn-oxide-based cathodes.

**APPROACH:** Our approach is to search for, characterize, and develop low-cost manganese oxide cathodes for Li-ion cells. We will continue to focus our work on high-voltage, high-capacity layered lithium-manganese oxide ‘composite’  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  structures with particular emphasis on electrodes in which  $\text{M}' = \text{Mn}$  and  $\text{M} = \text{Mn, Ni, Co}$  that operate between 3.0 and 4.8 V *vs.* Li<sup>0</sup>. These materials are showing excellent promise to replace LiCoO<sub>2</sub> as the cathode of choice for Li-ion batteries; they also hold promise for high-power applications. We will also attempt to exploit high-potential LiM<sub>2</sub>O<sub>4</sub> spinel materials (4.0-5.0 V *vs.* Li<sup>0</sup>) for high-power batteries. In conjunction with our anode project (Task 2.1), we will explore the electrochemical properties and the abuse tolerance of high-potential layered and spinel cathodes against graphite and low-potential metal oxide anodes.

**STATUS OCT. 1, 2004:** It was demonstrated that a rechargeable capacity of 170-180 mAh/g could be delivered by  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  composite electrodes in Li cells for 100 cycles between 4.5 and 3.0 V at 50°C. It was discovered that the irreversible capacity loss on the initial cycle could be reduced by pre-conditioning the electrodes with acid. A capacity in excess of 110 mAh/g was achieved from spinel electrodes when cycled between 5.0 and 3.5 V *vs.* Li which augers well for the development of stable high-voltage (>4.5 V) Li-ion cells. Evaluation of high-potential layered and spinel cathodes against metal oxide anodes had been initiated.

**STATUS SEPT. 30, 2005:** Improvements in the electrochemical performance of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  electrodes will have been achieved. High-capacity  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  layered electrodes and high-rate LiM<sub>2</sub>O<sub>4</sub> (4.0 – 5.0 V) spinel electrodes with a high Mn content will have been evaluated against graphite and metal oxide negative electrodes.

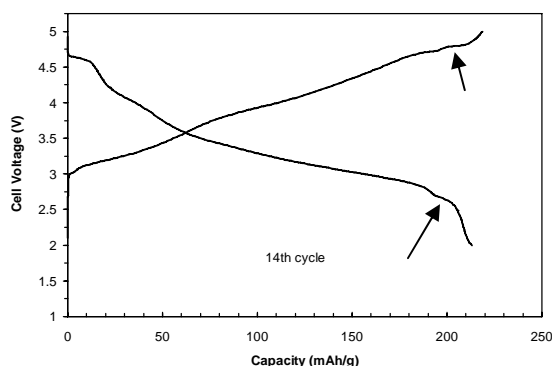
**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

**MILESTONES (by 30 September 2005):** 1) Evaluate  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  composite electrodes with a high Mn content against a technical target of 200 mAh/g for 100 cycles between 4.8 and 3.0 V *vs.* Li<sup>0</sup> at room temperature and at 50°C; 2) Evaluate the rate capability and low-temperature behavior of layered  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  and spinel LiM<sub>2</sub>O<sub>4</sub> electrodes; and 3) evaluate the layered and spinel cathodes against graphite and metal oxide anodes.

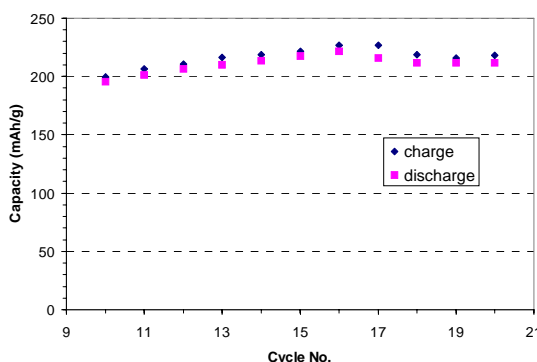
## PROGRESS TOWARD MILESTONES

We have been studying integrated ('composite') electrode structures with layered- and spinel components in the hope that we may be able to design a bi-functional electrode in which the layered component contributes predominantly to providing high capacity while the spinel component provides high power. Recent work on these high capacity (>200 mAh/g) electrodes was conducted on a hypothetical system with two layered components and one spinel component, denoted  $x\{\text{Li}_2\text{MnO}_3 \bullet \text{LiMO}_2\} \bullet (1-x)\text{LiM}_2\text{O}_4$ , in which M is predominantly Mn and Ni. Electrode precursors with a Li:Mn:Ni ratio of 4:3:1 that would correspond to a general formula  $0.5\{\text{Li}_2\text{MnO}_3 \bullet \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2\} \bullet 0.5\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  if all the manganese ions and all the nickel ions in the layered  $\{\text{Li}_2\text{MnO}_3 \bullet \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2\}$ -spinel  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  product were tetravalent and divalent, respectively, were prepared by firing stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$  at 900 °C in air.

Electrodes were cycled between 5 V and 2 V. Several break-in cycles were required to fully activate the electrode. A typical charge/discharge voltage profile of a  $\text{Li}/0.5\{\text{Li}_2\text{MnO}_3 \bullet \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2\} \bullet 0.5\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  cell is shown in Fig. 1. A rechargeable capacity greater than 200 mAh/g is achievable from these layered-spinel electrodes, as shown in Fig. 2 for cycles 10 to 20.



**Figure 1.** Voltage profile of a Li/layered-spinel cell.



**Figure 2.** Capacity vs. cycle no. plot

It is immediately clear from Fig. 1 that the  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  spinel component conveniently provides an indication of the approaching end-of-charge and end-of-discharge of the cell with voltage plateaus at approximately 4.8 V and 2.7 V, respectively (arrowed in Fig. 1). The voltage profile also indicates that the  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  spinel component seems to provide only ~12 mAh/g at 4.8 V and 2.7 V, suggesting that the distribution of the nickel and manganese ions in the layered and spinel components is significantly more complex than expected, and that the composition and concentration of spinel and layered components may vary across the electrode samples. For example, any increase in the Mn content of a layered  $\text{Li}[\text{Ni}_{0.5-y}\text{Mn}_{0.5+y}]\text{O}_2$  component or a  $\text{Li}[\text{Ni}_{0.5-z}\text{Mn}_{1.5+z}]\text{O}_4$  spinel component would necessitate trivalent  $\text{Mn}^{3+}$  ions in the starting electrode to maintain charge balance. It appears from Fig. 1 that the electrode may contain more than 50% of a layered component and/or a spinel component that provides a  $\text{Mn}^{4+/3+}$  couple at ~4.1 V during discharge. These observations emphasize the role that synthesis conditions may play in controlling the relative amounts of the layered- and spinel components in the electrode. We are continuing our investigations of these types of electrodes in an attempt to get greater clarity on their complex structural and electrochemical properties.

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Cathodes – Novel Materials

**SYSTEMS:** Li-Ion high voltage, high energy, and low-voltage/high stability

**BARRIER:** Lower-cost, higher-power, higher-capacity and abuse-tolerant safer cathodes

**OBJECTIVES:** The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials.

**APPROACH:** Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

**STATUS OCT. 1, 2004:** We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. Addition of other transition metals also prevents structure change at low Li content to one-block or spinel structures, and changes oxygen evolution behavior. We have completed an evaluation of  $\text{LiFePO}_4$  as a base-case low-cost cathode, and shown that it is intolerant of deep over-discharge. We also have shown that vanadium oxides can be stabilized by the addition of ammonium and manganese ions to attain capacities above 200Ah/kg.

- $\text{LiFePO}_4$ : > 120 Ah/kg for 100 cycles at 1 mA/cm<sup>2</sup>.
- Layered  $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$ : 175 Ah/kg and 150 Ah/kg for 30 cycles at 1 and 2 mA/cm<sup>2</sup> respectively.
- Layered  $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$  (A=  $\text{NH}_4$  or TMA):  $\geq 200$  Ah/kg for 6 cycles.

**STATUS SEPT. 30, 2005:** For low-cost Li-Ion cells, we expect to identify the changes in (a) electrochemistry, (b) oxygen evolution (abuse tolerance), (c) high rate capability (HEV), (d) coating effectiveness, and (e) the electronic conductivity of  $\text{LiMnO}_2$  structures as a function of substitution level as in  $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$ , so as to determine the optimum minimum substitution level. We will also have evaluated possible variants on iron phosphate as base-case cathodes, and explored some higher-capacity next-generation cathodes.

**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

**MILESTONES:** Our major milestones this year are: (a) to characterize the electronically stabilized manganese oxide, determine the optimum substitution of Mn to obtain a stable high-rate abuse-tolerant cathode (including application to HEV), and to compare the best samples with iron phosphates by July 2005, and (b) to search for, identify and characterize some new low-cost higher energy density cathode materials and to compare the best samples with the base-line chemistries (continuing).

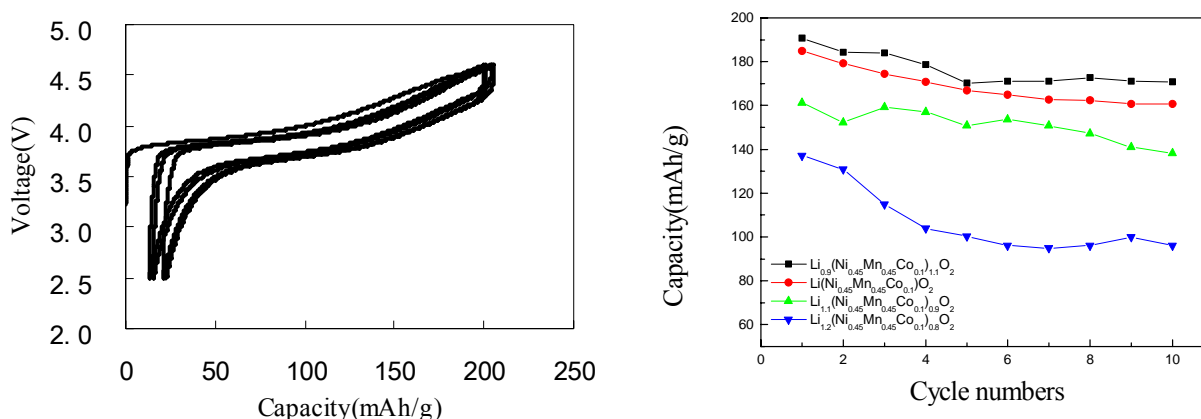
## PROGRESS TOWARD MILESTONES

Layered Lithium Manganese Dioxides. This Quarter we continued our studies of the layered lithium manganese nickel cobalt oxides. Specifically we evaluated the effect of changing the lithium content of the as-synthesized material for the low cobalt containing material:  $\text{Li}_y(\text{Mn}_{0.45}\text{Ni}_{0.45}\text{Co}_{0.1})_{2-y}\text{O}_2$  for  $0.9 \leq y \leq 1.2$ . Samples were synthesized at 800°C in air, structurally analyzed for nickel ordering, and evaluated in electrochemical cells. The results were somewhat surprising, with overall the compound with the lowest lithium content performing the best:

1. The lower the Li content, the lower the cell polarization on cycling.
2. The lower the Li content, the lower the first cycle capacity loss.
3. The lower the Li content, the higher the capacity for the first ten cycles.
4. The lower the Li content, the greater the Ni content on the Li sites.
5. The lower the Li content, the higher the magnetization hysteresis.

Figure 1 (a) shows the cycling of the sample with  $y=0.9$ , where 10% of the Li sites are occupied by Ni, the first cycle loss is only around 10 mAh/g and the polarization is about 100 mV. In contrast, for  $y=0.2$ , where less than 1% of the Li sites are occupied by Li, the first cycle loss is 90 mAh/g and the cell polarization over 200 mV. The cycling behavior of these materials is compared in Fig. 1 (b) for  $y$  from 0.9 to 1.2.

We are continuing our analysis of their thermal stability after partial Li removal. For the  $y=1$  material, when 30% of the Li is removed (=30% charge capacity), weight loss corresponding to oxygen loss begins at 150°C and is essentially complete by 350°C. In a collaborative study with C. Grey of Stony Brook, we are measuring the magnetic behavior of their  $\text{Li}_x\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  as a function of Li content; this should help in understanding the structural changes occurring on cycling.



**Figure 1.** (a) Cycling of Li in  $\text{Li}_y(\text{Mn}_{0.45}\text{Ni}_{0.45}\text{Co}_{0.1})_{2-y}\text{O}_2$  for  $y=0.9$  and (b) the capacity on cycling of  $\text{Li}_y(\text{Mn}_{0.45}\text{Ni}_{0.45}\text{Co}_{0.1})_{2-y}\text{O}_2$  as a function of  $y$ ; both at 0.5 mA/cm<sup>2</sup> from 2.5 to 4.6 volts.

**Further plans to meet or exceed milestones:** None

**Reason for changes from original milestones:** No changes

Publications and Presentations resulting from the work.

1. M.S. Whittingham, Y. Song, S. Lutta, P.Y. Zavalij and N. Chernova, "Some transition metal (oxy)phosphates and vanadium oxides for lithium batteries," *J. Materials Chem.* 15: 3362-3379 (2005).
2. Miaomiao Ma, Natasha A. Chernova, Peter Y. Zavalij, and M. Stanley Whittingham, "Structural and Electrochemical Properties of  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ ," *Mater. Res. Soc. Proc.* 835: K11.3 (2005).

## TASK STATUS REPORT

**PI, INSTITUTION:** M. Doeff, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

**SYSTEMS:** Low-voltage, high-stability ( $\text{LiFePO}_4$ ); high-voltage, high-energy ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , new manganese oxides); and high voltage, high-power (new manganese oxides)

**BARRIERS:** Cost, cycle life, safety, energy density, and power density

**OBJECTIVES:** To develop low-cost cathodes based on benign materials (manganese oxides, lithium iron phosphates, etc.) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCar.

**APPROACH:** Cathode materials are synthesized by various means. Physical and electrochemical properties (*e.g.*, structure, surface characteristics) are measured in conjunction with members of the diagnostic tasks. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

**STATUS OCT. 1, 2004:** Electrochemical characterization of  $\text{Li}_x\text{Al}_y\text{Mn}_{1-y}\text{O}_{2+z}$  O2/O3 intergrowths was completed. Experiments determining the optimum amount of pyromellitic acid (PA) for carbon-coating  $\text{LiFePO}_4$  were completed, and those using Fe promoters of graphene formation are underway.

**STATUS SEPT. 30, 2005:** Initial screening of novel manganese oxides for abuse-tolerance will be complete, and materials will be recommended for high-power applications based on results. *In situ* carbon structure, electrochemical performance, and synthetic parameters (*e.g.*, promoter-to-PA ratios) used in making coated  $\text{LiFePO}_4$  will be correlated. New manganese oxide structures without Ni or Co substituents for high-energy-density applications will continue to be surveyed.

**RELEVANT USABC GOALS:** 10-year life, < 20% capacity fade over a 10-year period.

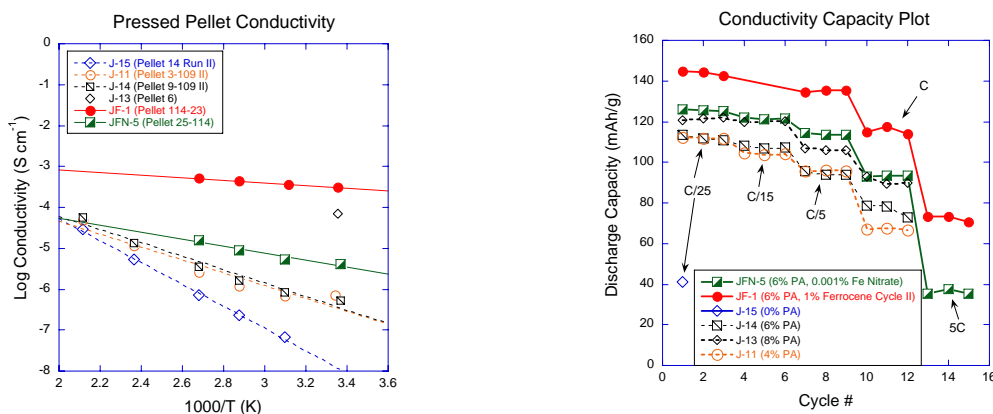
### MILESTONES:

- a) Determine best synthetic conditions (promoter-to-PA ratios, etc.) for carbon-coating  $\text{LiFePO}_4$ . (June 2005)
- b) Recommend the most abuse-tolerant manganese oxide structures for potential HEV applications, and highest energy density manganese oxides containing no Ni or Co for potential high-energy applications. (Sept. 2005)



## PROGRESS TOWARD MILESTONE (a)

(a) AC impedance measurements on cold isostatically pressed (CIP) pellets of  $\text{LiFePO}_4$  samples were carried out as a function of temperature. The results (Fig. 1a) mainly reflect the conductivities of the carbon at grain boundaries (particle surfaces). The correlation with cell performance (Fig. 1b) is striking. Further work will be directed towards further optimization of  $\text{LiFePO}_4/\text{C}$  composites and co-synthesis of carbon nanotubes with  $\text{LiFePO}_4$ .



**Figure 1a (left).** Conductivities as a function of temperature for several  $\text{LiFePO}_4$  samples.

**Figure 1b (right).** Capacity as a function of cycle number and rate for lithium cells containing the samples shown in Figure 1a.

(b) Elevated temperature cycling and storage tests on manganese oxides with tunnel structures were completed this quarter. In previous quarters,  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , a spinel manganese oxide, and layered manganese oxides were evaluated. Ti-containing manganese oxides with the  $\text{Na}_{0.44}\text{MnO}_2$  structure,  $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$  ( $x \approx 0.44$ ,  $0 < y \leq 0.55$ ), exhibit little or no capacity fading when cycled at  $55^\circ\text{C}$ . XRD, FTIR and electrochemical results are presently being evaluated to understand the elevated temperature behavior of all the manganese oxides studied.

**Further plans to meet or exceed milestones** N/A

**Reason for changes from original milestones** Milestone 4.3b postponed until Dec. '05 to finish evaluation of storage and cycling tests.

### Publications and Presentations

1) "Corrosion of Aluminum Current Collectors in Lithium-Ion Batteries," Xueyuan Zhang, Bryon Winget, Marca Doeff, James W. Evans, and Thomas M. Devine, *J. Electrochem. Soc.*, **152**, B448 (2005).

2) "Optimization of Carbon Coatings on  $\text{LiFePO}_4$ ," Polymer Battery and Fuel Cell 2, Las Vegas, NV, June 2005, Abstract 3.

## TASK STATUS REPORT

**PI, INSTITUTION:** J.B. Goodenough, University of Texas at Austin

**TASK TITLE - PROJECT:** Cathodes - Novel Materials

**SYSTEMS:** Li secondary battery

**BARRIERS:** Cost, cycle life, safety, and energy density

**OBJECTIVES:** To evaluate alternative *cathode* materials for a lithium-ion battery.

**APPROACH:** The universal motif of cathodes in rocking chair  $\text{Li}^+$ -ion batteries is one of immobilized redox centers that are accessible to electrons from the current collector and  $\text{Li}^+$  ions from the electrolyte. Immobilization ensures that the redox units do not transfer to and subsequently poison the anode. Our research is centered around high-power cathodes for the purpose of EV and HEV's. This translates into pure or composite materials which allow for transfer of electrons *and*  $\text{Li}^+$  ion with little or no resistance. We are currently pursuing three different avenues of research: (1) new materials based on conventional oxide structures with proven high rate capabilities, (2) new cathode schemes based on conductive polymers which may serve either as self-contained cathodes or as a new conductive binder in more conventional composite cathodes, and (3) substitution into the environmentally benign and cost-effective  $\text{LiFePO}_4$  to improve rate capabilities.

**STATUS OCT. 1, 2004:** Well-ordered  $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$  has been prepared and battery testing has shown good cyclability. A principle for predicting cation order/disorder in layered materials with an  $\alpha\text{-NaFeO}_2$  structure has been developed. Preliminary rate tests are in progress.

**STATUS SEPT. 30, 2005:**

- Electrochemical testing of our high-rate layered material to elucidate the limiting parameter will have been completed.
- Preliminary analysis of substitution into the Fe site of  $\text{LiFePO}_4$  will have been completed.
- The feasibility of polypyrrole as a conducting binder/scaffolding will have been explored.

**RELEVANT USABC GOALS:** 10-year life, < 20% capacity fade over a 10-year period.

**MILESTONES:**

1. Electrochemical testing of our high-rate layered material to elucidate the limiting parameter. (Feb. 2005)
2. Preliminary analysis of substitution into the Fe site of  $\text{LiFePO}_4$ . (Aug. 2005)

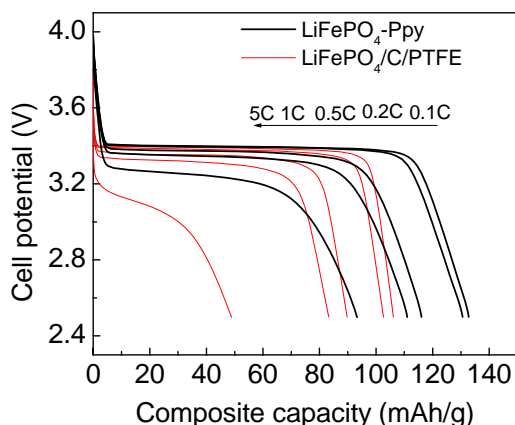
## PROGRESS TOWARD MILESTONES

In our previous work, we found enhanced composite capacity and rate capability in an electrodeposited  $\text{LiFePO}_4$ /polypyrrole(Ppy) composite cathode in which the conventional additives C-black and Teflon were replaced by Ppy. In the past quarter, we repeated and optimized the experiment; we also noted that a carbon coating of the particles is needed for binding to the Ppy.

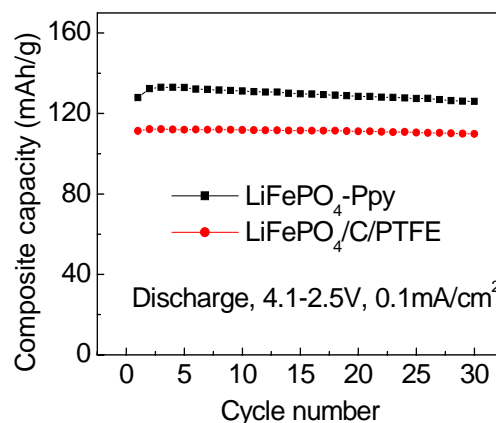
$\text{LiFePO}_4$  provided by Phostech Company was used as the starting material for the  $\text{LiFePO}_4$ /Ppy composite cathode. As shown in Fig. 1,  $\text{LiFePO}_4$ /Ppy exhibits a significantly enhanced composite capacity compared with conventional  $\text{LiFePO}_4$ /C/PTFE. On discharging at the same current density, the plateau caused by the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple in  $\text{LiFePO}_4$ /Ppy is broadened and the overpotential is reduced (the cell resistance decreases). Notably,  $\text{LiFePO}_4$ /Ppy performs well even at high discharge currents, *e.g.*, 5C. Furthermore, it is stable over redox cycling. After 30 cycles, the capacity loses about 5%, as displayed in Fig. 2. The capacity of  $\text{LiFePO}_4$ /Ppy is about 20% higher than that of  $\text{LiFePO}_4$ /C/PTFE at 0.1  $\text{mA}/\text{cm}^2$ . At higher current density, the difference in capacity is significantly larger. Recent independent reports of  $\text{LiFePO}_4$ /Ppy composites prepared by a chemical route and mechanical mixing gave a much poorer result. We have now optimized the condition for cathode fabrication by electrochemical deposition.

Since Phostech  $\text{LiFePO}_4$  contains a small amount of coated carbon, we designed several experiments in order to investigate the role of the coated carbon. Addition of any amount of conductive C-black in the solution for electrodeposition led to a collapse in performance of the composite cathode. We also prepared  $\text{LiFePO}_4$  fine particles at 200°C via a novel solvothermal method to avoid any *in situ* coated carbon to replace the Phostech  $\text{LiFePO}_4$  for the composite cathode fabrication. But we only obtained a composite capacity of less than 20  $\text{mAh}/\text{g}$  even though the solvothermal-obtained  $\text{LiFePO}_4$  with conventional additives showed a capacity of 130  $\text{mAh}/\text{g}$ . We conclude that the coated carbon in Phostech  $\text{LiFePO}_4$  plays an important role in the electrodeposition process of the composite cathode. Probably the coated carbon promotes the *in situ* adsorption of the  $\text{LiFePO}_4$  particles to the Ppy on the steel mesh.

In the next quarter, we will further investigate the fabrication and performance of  $\text{LiFePO}_4$ /Ppy composite cathodes and also try this strategy with other oxides, *e.g.*,  $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ .



**Figure 1.** Cell potential vs composite capacity on discharging at different currents.



**Figure 2.** Variation of composite capacity with cycling for  $\text{LiFePO}_4$ -Ppy and  $\text{LiFePO}_4$ .

## TASK STATUS REPORT

**PI, INSTITUTION:** A. Manthiram, University of Texas at Austin

**TASK TITLE - PROJECT:** Cathodes - Superior Capacity Retention, High-Rate Spinel Manganese Oxide Compositions

**SYSTEMS:** Spinel manganese oxides

**BARRIERS:** Cycle life, elevated-temperature storage, power density, and energy density

**OBJECTIVES:** To develop low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high rate, low irreversible capacity loss, and good storage characteristics at elevated temperatures.

**APPROACH:** Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions as well as an optimization of the microstructure and morphology are being pursued.

**STATUS OCT. 1, 2004:** A variety of multiple cationic substitutions in the spinel  $\text{LiMn}_2\text{O}_4$  system and an evaluation of the electrochemical performances of the various compositions have established a clear correlation of the electrochemical properties to some basic materials parameters such as the initial manganese valence and the lattice parameter difference  $\Delta a$  between the two cubic phases formed during the charge-charge process.

**STATUS SEPT. 30, 2005:** Evaluation of the optimized  $\text{LiMn}_{2-y-z}\text{Ni}_y\text{Li}_z\text{O}_4$  and  $\text{LiMn}_{2-y-z-\eta}\text{M}_y\text{Li}_z\text{M}'_\eta\text{O}_4$  (M and M' = transition and non-transition metal ions) spinel oxide compositions (4 V) in Li-ion cells, identification of the factors that control the electrochemical performances of the cation-substituted 5 V spinel oxide system  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , and a comparison of the factors with those of the 4 V spinel oxide cathodes.

**RELEVANT USABC GOALS:** 10-year life, < 20 % capacity fade over a 10-year period

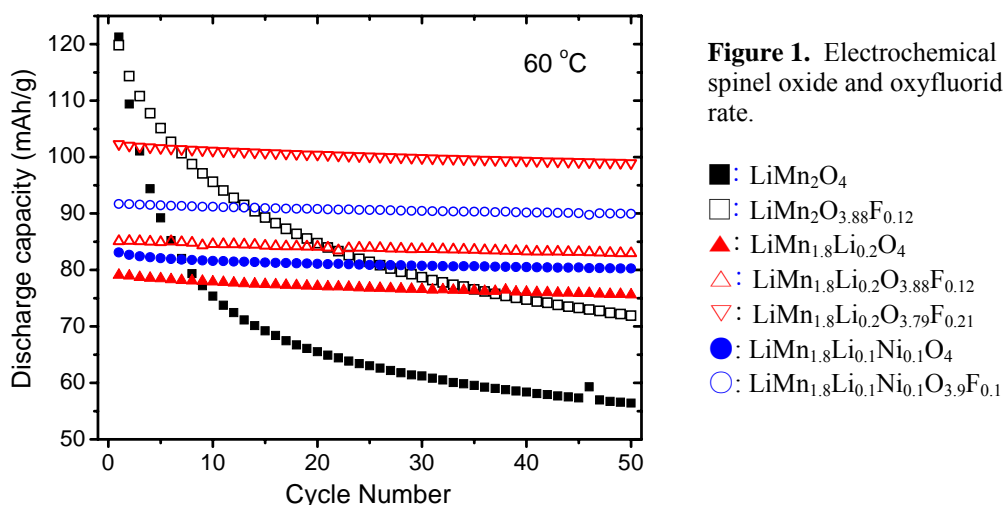
### MILESTONES:

1. Evaluation of the optimized 4 V spinel oxide cathodes in Li-ion cells. (Mar. 2005)
2. Identification of the factors controlling the electrochemical performances of the cation-substituted 5 V spinel oxide system  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ . (Sept. 2005)

## PROGRESS TOWARD MILESTONES

Our previous work indicated that fluorine substituted spinel oxide compositions exhibit a combination of superior capacity retention and storage characteristics with a lower amount of manganese dissolution than the corresponding oxide analogs. However, the amount of fluorine incorporated into the lattice is strongly influenced by the synthesis conditions (temperature and time) due to the volatilization of fluorine at elevated temperatures. With an aim to maximize the fluorine content, we have now adopted a procedure in which the cation-substituted oxides already synthesized at higher temperatures ( $\sim 800^\circ\text{C}$ ) is fired with ammonium hydrogen fluoride at a moderate temperature of  $450^\circ\text{C}$  for 5 h. Adopting this procedure, we have synthesized compositions such as  $\text{LiMn}_2\text{O}_{4-z}\text{F}_z$ ,  $\text{LiMn}_{1.8}\text{Li}_{0.2}\text{O}_{4-z}\text{F}_z$ , and  $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-z}\text{F}_z$ . Based on the analysis of the oxidation state of the transition metal ions by a redox titration and an assumption of the total anion (O + F) content to be 4.0, we have been able to incorporate fluorine contents  $0 \leq z \leq 0.2$  into the lattice. The fluorine substituted oxyfluoride spinel compositions thus synthesized exhibit 8-20 mAh/g higher capacities than the corresponding oxide counterparts as seen in Fig. 1 due to a lowering of the oxidation state of manganese. They also exhibit better cyclability at  $60^\circ\text{C}$  than the oxide analogs (Fig. 1) while maintaining similar rate capabilities. The better electrochemical performance of the oxyfluoride cathodes is found to be due to a smaller lattice parameter difference  $\Delta a$  between the two cubic phases formed during the charge-discharge process and a lower degree of manganese dissolution compared to the corresponding oxide analogs. Manganese dissolution evaluated by soaking the sample powders in 1 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate electrolyte at  $55^\circ\text{C}$  for 7 days indicates up to a 30% reduction in manganese dissolution on going from an oxide to the corresponding oxyfluoride. We are currently in the process of evaluating the storage characteristics of the oxyfluoride samples.

Additionally, we have compared the amount of transition metal ion (Mn, Co, Ni, and Fe) dissolution in spinel, layered, and olivine oxides to develop a broader understanding of the impact of metal ion dissolution in cathodes. Layered and spinel oxides containing  $\text{Mn}^{4+}$  such as  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  show lower manganese dissolution than spinel  $\text{LiMn}_2\text{O}_4$  and orthorhombic  $\text{LiMnO}_2$  containing  $\text{Mn}^{3+}$ , suggesting that the degree of manganese dissolution is related to the presence of  $\text{Mn}^{3+}$ . Interestingly, despite the presence of  $\text{Mn}^{3+}$ , the cation-substituted oxide and oxyfluoride spinel compositions such as  $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.075}\text{O}_4$  and  $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.075}\text{O}_{3.8}\text{F}_{0.2}$  exhibit much reduced manganese dissolution but slightly higher than that found with the  $\text{Mn}^{4+}$  containing spinel cathodes.



**Figure 1.** Electrochemical cycling performances of spinel oxide and oxyfluoride cathodes at  $60^\circ\text{C}$  at C/5 rate.

## BATT TASK 5 DIAGNOSTICS

### TASK STATUS REPORT

**PI, INSTITUTION:** R. Kostecki, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Electrode Surface Layers

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>,  
High-voltage, high-power: Gr/LiBOB+γBL:EA:LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Short lithium battery calendar/cycle lifetimes.

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface chemistry, interfacial phenomena, and cell power or capacity decline.

**APPROACH:** Our approach is to use *in-situ* and *ex-situ* Raman microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film or single-particle model electrodes. Data to be collected include changes in electrode surface morphology, structure, electronic conductivity, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

**STATUS OCT. 1, 2004:** We expect to develop better understanding of the mechanism of carbon retreat in the composite LiAl<sub>0.05</sub>Ni<sub>0.8</sub>Co<sub>0.15</sub>O<sub>2</sub> cathodes and its impact on the cathode electrochemical performance upon cycling and storage in LiPF<sub>6</sub>-EC-EMC electrolyte at elevated temperatures. We intend to identify and characterize physico-chemical processes, which are responsible for this effect, and establish possible links with other detrimental phenomena. The correlations between electrode history, electrode surface properties, and temperature for baseline LiAl<sub>0.05</sub>Ni<sub>0.8</sub>Co<sub>0.15</sub>O<sub>2</sub> cathodes will be developed. We expect to determine and verify the key elements for high-rate performance of LiFePO<sub>4</sub> composite cathodes, *i.e.*, the effect of residual carbon and solid-solution doping by metals supervalent to Li<sup>+</sup>.

**STATUS SEPT. 30, 2005:** We expect to define relationships between electrochemical performance and limitations of BATT baseline systems and cell history, abuse tolerance, electrodes surface properties, and interfacial phenomena. We intend to develop good understanding of the key elements for good electrochemical performance of LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> composite cathodes. We anticipate determining the mechanism of graphite disordering in composite anodes and carbon retreat in composite cathodes, and evaluate their impacts on long-term Li-ion cell performance. We also expect to develop an experimental methodology to carry out exploratory *in-situ* spectroscopy and microscopy studies of single-particle electrodes to characterize BATT baseline electrode materials.

**RELEVANT USABC GOALS:** 15 year life, 30 ohm-cm<sup>2</sup> area-specific impedance, 300,000 shallow discharge cycles.

**MILESTONES:** (a) Quantitative and qualitative analysis of carbon retreat from composite cathodes by <sup>13</sup>C distribution examination in model Li-ion cells by March 2005. (b) Preliminary evaluation of *in-situ* microwave-assisted synthesis of graphitic carbon matrix for composite cathodes by June 2005.

## PROGRESS TOWARD MILESTONES

Our primary objective in the second quarter of FY05 was to fully evaluate the direct *in situ* microwave-assisted synthesis of graphitic carbon matrix for composite cathodes to improve high-rate and cycle performance of Li-ion batteries. Improved electrochemical performance of  $\text{LiFePO}_4$  is associated with the presence of  $\text{sp}^2$ -coordinated carbon coatings, which exhibit better electronic conductivity than disordered and/or  $\text{sp}^3$ -coordinated carbonaceous materials (collaboration with Marca Doeff, LBNL). However, simple pyrolysis of organic precursors at temperatures below  $800^\circ\text{C}$  yields highly amorphous and poorly conductive carbons. Microwave plasma assisted chemical vapor deposition (MPACVD) is used commercially to produce diamond coatings from  $\text{CH}_4/\text{H}_2$  gas mixtures. To obtain graphite-like coatings a different type of organic precursors with high C/H ratio (*e.g.*, naphthalene, anthracene etc.) must be used. Interaction with low-pressure (1-2 mTorr) Ar-plasma and strong electromagnetic radiation lead to vaporization and immediate pyrolysis (1-5 seconds) of the organic precursor at relatively low temperatures. The SEM and HRTEM images of MPACVD carbon films reveal densely packed  $\sim 50$  nm primary particles with individual graphene domains reaching  $\sim 50$  Å, *i.e.*, domain sizes typical for carbonaceous materials pyrolyzed at temperatures  $>1200^\circ\text{C}$ . Excellent electronic conductivity of these thin carbon films ( $\sim 2 \text{ Scm}^{-1}$ ) was confirmed in a series of four-point probe measurements. On the other hand, XRD and Raman spectroscopy provide no evidence of structural degradation in  $\text{LiFePO}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Al}_{0.05}\text{O}_2$  powders after MPACVD processing. Preliminary electrochemical tests of MPACVD carbon-coated composite  $\text{LiFePO}_4$  electrodes (collaboration with Karim Zaghib, HQ-IREQ) reveal substantial improvement in active material utilization and power performance.

Our second objective was to continue to study in detail the carbon additive retreat in composite cathodes and its possible implications for battery performance. A new set of  $^{13}\text{C}$ -enriched composite  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathodes were manufactured and characterized. We used a new type of  $^{13}\text{C}$  soft carbon, which emulates properties of acetylene black better than hard carbon  $^{13}\text{C}$  that we used in our previous experiments. Electrochemical calendar life/cycle life tests of these cells at room temperature and at  $45^\circ\text{C}$  are currently being carried out. We expect to accomplish the milestone (a) in the FY 2006. The delay is mainly caused by time-consuming processes of  $^{13}\text{C}$  isotope screening, electrode manufacturing, cell assembly/optimization, and long life/cycle testing.

Our third objective was to investigate the mechanism of interfacial impedance rise in composite cathodes during storage in organic carbonate-based electrolytes at elevated temperatures. Al/carbon black,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiFePO}_4$  composite electrodes were manufactured, dried under vacuum at  $120^\circ\text{C}$  for 6, 12 and 42 hours, and subsequently stored in 1.2 M  $\text{LiPF}_6$ , EC:EMC 3:7 vol%. The electrodes were stored in fully discharged state at open circuit potential at  $45^\circ\text{C}$  in a He-filled glove box. Electrochemical impedance tests reveal that (i) the electrodes' initial interfacial impedance depends strongly on the heat treatment time, (ii) the rate of impedance rise upon prolonged storage in the electrolyte at elevated temperatures is pre-determined by the heat treatment parameters *i.e.*, temperature, pressure, and time, (iii) Al/carbon black,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ,  $\text{LiFePO}_4$  composite electrodes display similar impedance behavior. These results indicate that the impedance of the composite electrodes is rather independent of the nature of the cathode active material but depends strongly on the carbon additive behavior. SEM, EDX, Raman and FTIR measurements of aged electrodes exhibit  $\text{LiF}$ ,  $\text{Li}_x\text{PF}_y$ ,  $\text{Li}_x\text{PF}_y\text{O}_z$ , and alkyl carbonates compounds on the surface of all aged electrodes. Adsorbed  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $-\text{C}-\text{O}-\text{H}$ ,  $-\text{C}=\text{O}$  surface functional groups present on carbon additive react with the electrolyte. We postulate that these side-reaction products create electronic barriers in the composite electrode, which contribute to the impedance of the composite electrodes.

## TASK STATUS REPORT

**PI, INSTITUTION:** W.-S. Yoon and X.-Q. Yang, Brookhaven National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Battery Materials: Structure and Characterization

**SYSTEMS:** High-power Li-ion, high-energy Li-ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective is to determine the contributions of electrode material changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline. The results of these studies will be used to guide exploratory research for new cathode, anode, and electrolyte materials for high-power Li batteries.

**APPROACH:** Our approach is to use a combination of *in situ*, *ex situ*, and time-resolved synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish between surface and bulk processes on electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. Hard and soft XAS will be used to elucidate the charge-compensation mechanisms for cathode materials during electrochemical cycling. This work will be carried out in collaboration with other BATT members.

**STATUS OCT. 1, 2004:** In FY 2004 comparative studies between Gen2 ( $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ) cathode and  $\text{LiMn}_2\text{O}_4$  spinel cathode have been completed using *in situ* X-ray diffraction (XRD) technique. Both cathodes were cycled at room temperature and 55°C. We have developed time-resolved XRD techniques using image plate detectors (IPD), and the thermal stability study of cathode materials at elevated temperatures in the presence of electrolyte is ongoing. We completed the *in situ* hard X-ray XAS and XRD work on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrodes. Synchrotron based X-ray studies on the effect of new electrolytes and additives on the stability of  $\text{LiMn}_2\text{O}_4$  electrodes at elevated temperatures are ongoing.

**STATUS SEPT. 30, 2005:** We expect to complete the *ex situ* soft X-ray XAS work on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrodes during the cycling process. We also expect to complete the *in situ* XRD work on  $\text{LiFePO}_4$  during electrochemical cycling at elevated temperatures. *In situ* XRD work on surface-coated  $\text{LiMn}_2\text{O}_4$  spinel cathode materials will be completed. Soft X-ray XAS using partial electron yield and fluorescence yield detectors will be applied to various cathode materials at the O, F, and P K edges and at the  $L_3$  and  $L_2$  edges of the 3d transition metals.

**RELEVANT USABC GOALS:** 15 year life, < 20% capacity fade over a 10-year period.

### MILESTONES:

- 1) Complete *ex situ* soft X-ray XAS on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , during cycling. (Apr. 2005)
- 2) Complete *in situ* XRD work on surface-coated  $\text{LiMn}_2\text{O}_4$  spinel cathode materials. (Oct. 2005)



## PROGRESS TOWARD MILESTONES

Soft x-ray (200 eV to 1000 eV) absorption spectroscopy (XAS) was used to study the mechanism of power fading of cathode materials. Soft x-ray XAS probing the elements with absorption edges between 200 and 1000 eV (*e.g.*, the K edges of O and F) can provide information about both surface and bulk. Our previous results using *in situ* XRD showed that the changes at the surface of electrode is very important in studying the capacity fade and power fade. The formation of LiF at the surface of  $\text{LiMn}_2\text{O}_4$  during cycling may play an important role in  $\text{LiMn}_2\text{O}_4$  cathode deterioration, based on the fact that the fading was improved by using additive with LiF dissolving power in the electrolyte. Soft X-ray absorption studies at F K-edge confirm that LiF is formed on the surface of  $\text{LiMn}_2\text{O}_4$  during cycling. We have prepared binder-free thin film  $\text{LiMn}_2\text{O}_4$  electrodes in order to eliminate the interference caused by the fluorine in PVdF on the F K-edge spectra. The soft X-ray absorption spectra were collected from samples at various charge states as the cell underwent

3 to 4.5 V charge, followed by a discharge to 2.0 V, in comparison with another cell that underwent cycling between 3.0 and 4.5 V for seven times. Distinct signature of LiF was observed between the sample at 4.5 V after the first charge and that at 2.0V after the first discharge. In the sample charged to 4.5 V, the signature of LiF is very weak and similar to that of the pristine sample, while significant increase of the LiF signature was observed after the first discharge to 2.0V. It looks like that the formation of LiF at the surface of  $\text{LiMn}_2\text{O}_4$  takes place primarily during discharge.

We have continued the *in situ* time-resolved XRD study to monitor temperature-induced structural changes in carbon-coated  $\text{LiFePO}_4$  provided by Dr. Zaghib in Hydro-Québec. The structure of the charged  $\text{Li}_{1-x}\text{FePO}_4$  cathode is much more thermally stable than the layered  $\text{LiNiMnO}_2$ . The thermal decomposition of a series of iron phosphate cathode materials, in comparison with

$\text{Li}_{1-x}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$  and Gen2 ( $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ) cathodes at different charged state, was studied during heating from 25 to 450°C with and without electrolyte. Comparing the time resolved XRD spectra plotted in Fig. 1, it can be seen that the decomposition temperature is about 420°C for the  $\text{Li}_{0.05}\text{FePO}_4$  at 100% state of charge (SOC). This temperature is about 310°C for the  $\text{Li}_{0.35}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  cathode at the same SOC. These results provide clear correlation between the thermal stability and the structural changes of the cathode materials when heated to high temperatures.

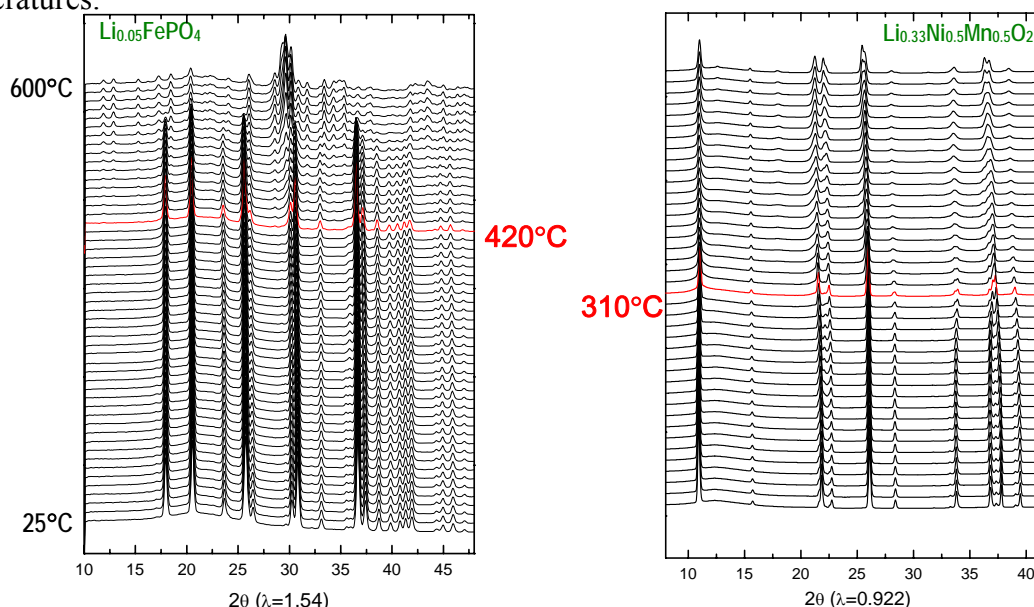


Figure 1. Time-resolved XRD patterns for  $\text{Li}_{0.05}\text{FePO}_4$  and  $\text{Li}_{0.35}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  in the absence of electrolyte, when heated from 25°C to 600°C

## TASK STATUS REPORT

**PI, INSTITUTION:** P.N. Ross, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics – Interfacial and Reactivity Studies

**SYSTEMS:** High Power Battery

**BARRIER:** Short battery lifetime

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

**APPROACH:** Our approach is to use in-situ Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. Model systems to be studied this year include new Mn-based cathode materials and new Sb-based anodes. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

**ANTICIPATED STATUS OCT. 1, 2004:** The oxidation and reduction chemistry of the new Li-ion battery electrolyte salts, LiBOB has been determined. The oxidative stability of GEN2 Li-ion battery electrolyte with the new Mn-based cathodes materials has been determined. The composition of the SEI layer on Sb-based anodes in PC-based electrolyte is under investigation.

**STATUS SEPT. 30, 2005:** The composition and stability of the SEI layer on Sb-based anodes in PC-based electrolyte will be known. The predicted advantages of a Sb-based anode vs. carbon/graphite anode for the high power battery application will be established. Irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature will be determined.

**RELEVANT USABC GOALS:** 15-year life, < 20% capacity fade over a 15-year period.

### MILESTONES:

- 1) Determine the potential advantages of a Sb-based anode vs. carbon/graphite anode for the high power battery application based on differences in composition and stability of the SEI layer. (May 2005)
- 2) Determine the nature of irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature. (Sept. 2005)

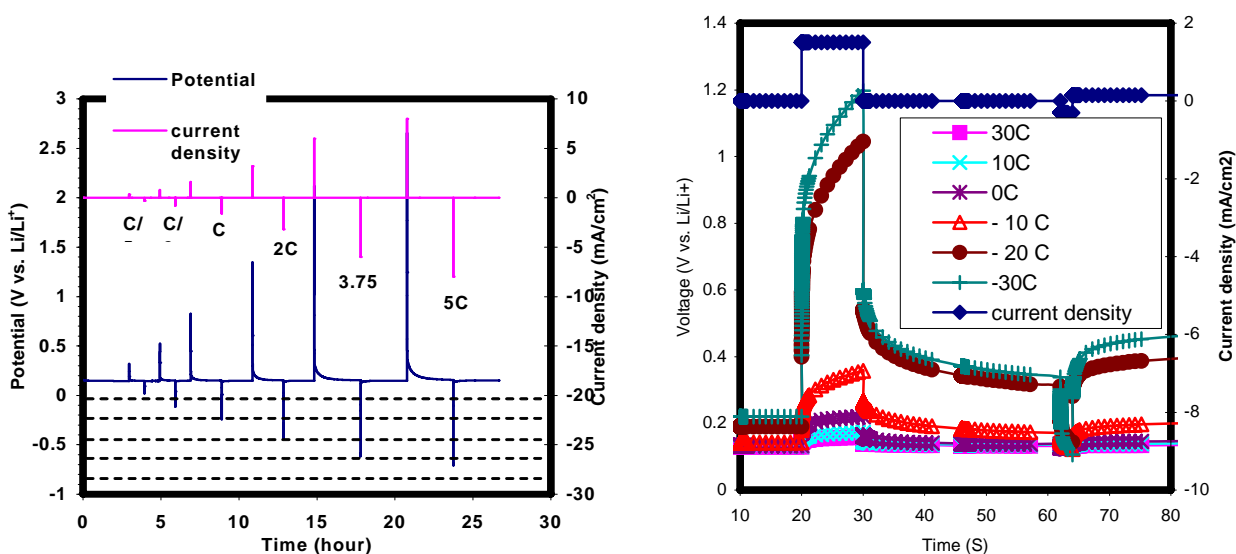
## PROGRESS TOWARDS MILESTONES

### Interfacial Chemistry at Low Temperature

We continue the study of interfacial chemistry in Li-ion batteries at low temperature. The experiments in this quarter focused on interfacial phenomena observed with GEN2 anodes (MAG-10) in GEN2 electrolyte as a function of current density of charge/discharge at  $-30^{\circ}\text{C}$ . Swagelok cells were used with Li counter electrodes and *ex situ* analysis of the graphite anodes using a combination of FTIR and XPS. In parallel, experiments on Li deposition on non-carbon (Ni) electrodes were done in the same electrolytes to establish the FTIR signatures of the SEI layer on metallic Li versus graphite in these electrolytes. The graphite anodes went through formation cycling at low rate (C/25) at room temperature followed by HPPC testing at 50 DOD. The cell was then placed in the environmental chamber at  $-30^{\circ}\text{C}$ , subjected to variable charge/discharge profile

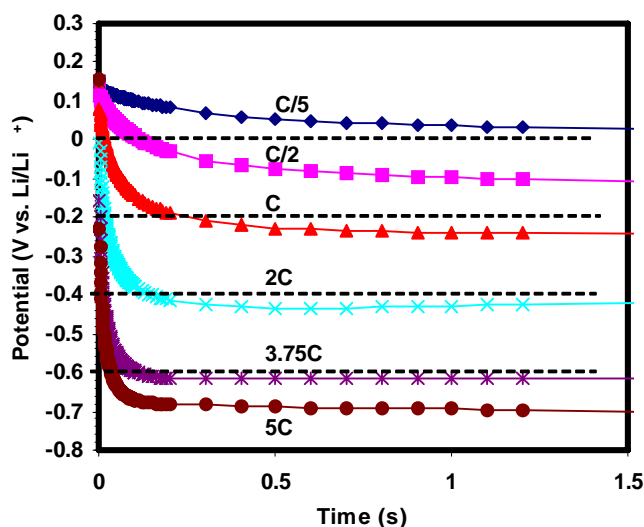
testing at  $-30^{\circ}\text{C}$ , then returned to room temperature, and HPPC tested again before the electrodes were removed from the cells and examined by FTIR.

Figure 1 shows the results at  $-30^{\circ}\text{C}$  from a symmetric charge/discharge pulse (5 sec) profile with progressively increasing current density. The polarization on discharge becomes larger than that on charge above about the C-rate. Lithium deposition probably does not occur until the 2C rate and higher (if it occurs at all). Figure 2 shows further study of the effect of temperature and details of the polarization on discharge. The polarization increases dramatically below ca.  $-10^{\circ}\text{C}$  and has a dramatically large range of characteristic time constants, some very slow (many seconds), at  $-30^{\circ}\text{C}$  (Fig. 3). In contrast the time constants for the polarization on charge are much faster, less than 0.2 seconds even at  $-30^{\circ}\text{C}$ . However, to our surprise, following return of the cells to room temperature, and post mortem by FTIR analysis, there were no “fingerprints” characteristic of Li deposition on these electrodes (experiments were repeated 4 times) in contrast to results we had reported previously. We have no explanation for this result at this time.



**Figure 1.** Potential response to symmetric discharge/charge pulses (5 sec) at increasing rates

**Figure 2.** Polarization as a function of temperature at C-rate discharge and C/5 charge



**Figure 3.** Polarization at  $-30^{\circ}\text{C}$  as a function of rate

## TASK STATUS REPORT

**PI, INSTITUTION:** G. Ceder, Massachusetts Institute of Technology  
C. Grey, SUNY at Stony Brook

**TASK TITLE - PROJECT:** Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials

**SYSTEMS:** Doped lithium nickel manganese oxides; lithium iron phosphates

**BARRIERS:** Low rate capabilities, high cost, poor stability.

**OBJECTIVES:** Determine the effect of structure on stability of cathodes. Explore rate limitations and relation to structure.

**APPROACH:** Use solid-state NMR to characterize local and diffraction/TEM for long-range structure, as a function of sample preparation method, state of charge, and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, and the effect of structure on cell voltages; and to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low-activation energy pathways for cation migration and to investigate electronic conductivity.

**STATUS OCT. 1, 2004:** The analysis of the local and long-range structures of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (calculations, diffraction, and NMR) will have been completed. NMR studies of local structure of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  following extended cycling studies will have been completed.

**STATUS SEPT. 30, 2005:** Correlations between  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  local and long-range structure and stability will have been completed. Joint NMR/calculations of conduction mechanisms (ionic and electronic) of BATT cathode materials will be underway. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT program will be ongoing.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade

### MILESTONES:

- 1) Complete analysis of x-ray and neutron diffraction of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ . Perform initial tests on conductivity model. (Nov. 1, 2004)
- 2) Complete analysis (NMR, TEM, diffraction) of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  as a function of synthesis method. Examine effect of structure on  $\text{Li}^+$  mobility in  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (calculations/NMR); extension of approach to other BATT systems will be underway. Complete studies of acid-leached  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (Thackeray) and  $\text{Ni}^{3+}$ -doped material (Goodenough). Outline and perform initial test of stability prediction methodology. (May 1, 2005).

## PROGRESS TOWARD MILESTONES

After developing the structural models for  $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$  we are now using it to understand two other aspects of the material: its rate capability and its structural changes upon cycling. TEM has been performed on materials cycled to various voltages. In previous work we had predicted that Ni, Mn and Li would form a complex ordering patterns in the transition metal layer (flower ordering) and that this ordering pattern is responsible for limiting the capacity to 220 mAh/g. We have observed reflections indicative of this superstructure in TEM and synchrotron X-ray diffraction but find now that upon very high charge (to 5.3V), leading to almost all the removal of the Li ions ( $^6\text{Li}$  NMR results; Fig. 1), these superstructure reflections disappear, indicating that such a deep charge also modifies the ordering of ions in the transition metal layers. We are in the process of correlating these changes with a model for ionic disorder in the material.

Using first principles modeling we have started to investigate why the rate capability of this material is poor. Preliminary calculations indicate that this is not due to the electrostatic interaction with the Ni ions that are present in the Li layer as is often assumed.

Rate studies in  $\text{LiFePO}_4$  have also been initiated. We have developed the first ab-initio technique to compute the migration barrier for polarons in full ab-initio plane wave calculations in solids. This

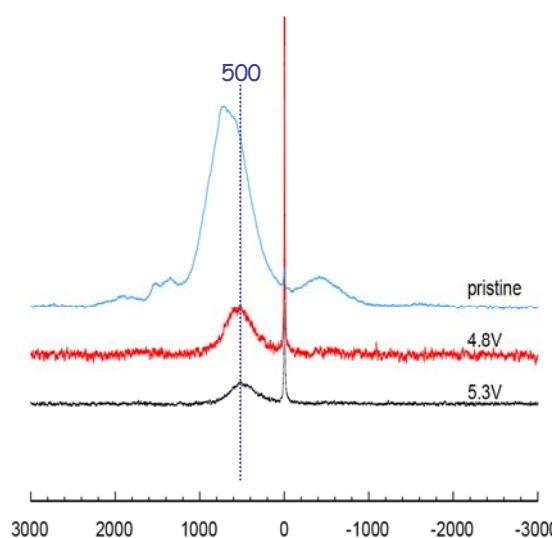


Figure 1.  $^6\text{Li}$  MAS NMR results show that 90% of the  $\text{Li}^+$ -ions are lost on charging to 5.3V.

makes it possible to investigate intrinsic electronic mobility in  $\text{LiFePO}_4$  and  $\text{FePO}_4$ . We find that mobility should be higher in  $\text{FePO}_4$  than in  $\text{LiFePO}_4$ . This is in agreement with what is obtained by Srinivasan by fitting transport models to charge discharge curves of  $\text{LiFePO}_4$ . While the activation barriers for polarons are not excessively high in  $(\text{Li})\text{FePO}_4$  we find a strong binding with  $\text{Li}^+$  ions.

We have made significant progress on developing an ab-initio modeling technique to predict the stability of electrode materials at the top of charge. We have benchmarked our method against the oxidation enthalpy for many known transition metals and have started calculations on  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNiO}_2$ . These systems are chosen as benchmarks because good experimental data on their decomposition at TOC is available.

Figure 1 shows the computed phase diagram (stable phases at low temperature for Li-Ni-oxides). This can be used to predict the reaction path for the decomposition of highly charged  $\text{LiNiO}_2$ . We will continue our efforts in this area and predict the stability of newer cathode materials.

## TASK STATUS REPORT

**PI, INSTITUTION:** T.M. Devine, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Diagnostics – Corrosion of Current Collectors

**SYSTEMS:** Low-cost Li-ion

**BARRIERS:** Uncertain and possibly inadequate corrosion resistance of Al current collectors

**OBJECTIVES:** Determine the influence of corrosion and passivation of Al current collectors on the capacity loss of Li-ion batteries. Determine the effect of water contamination of battery electrolytes on the corrosion and passivation of Al current collectors. Compare/contrast the corrosion and passivation of Al in battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$ .

**APPROACH:** This project consists of three tasks, which are worked on in parallel. In Task 1, the influence of corrosion and passivation of Al current collectors on battery capacity loss is quantitatively evaluated. Three conditions of the Al current collectors are investigated: 1) Al covered with an air-formed film of  $\text{Al}_2\text{O}_3$ , which is the current collector's surface condition in an unused battery; 2) Al covered with a duplex surface film consisting of an inner layer of air-formed  $\text{Al}_2\text{O}_3$  and an outer layer of  $\text{AlF}_3$ , which is the surface condition that might develop after a number of charge/discharge cycles in  $\text{LiPF}_6$  electrolytes; 3) Al covered with a 1- $\mu\text{m}$  thick anodized film of  $\text{Al}_2\text{O}_3$ , which is a surface condition that earlier work has shown to exhibit excellent corrosion resistance. In all three cases the current collectors are coated with cathodes of  $\text{LiFePO}_4$ . In Task 2, concentrations of water ranging from 2 to 100 ppm are deliberately added to battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$  to investigate the influence of water contamination on the corrosion and passivation of Al current collectors. In Task 3, electrochemical tests and *in situ* Raman spectroscopy are employed to probe the mechanism of corrosion of Al current collectors. Task 3 provides the mechanistic understanding of the corrosion phenomena that contribute to battery capacity loss as determined in Task 1.

**STATUS OCT. 1, 2004:** Aluminum electrodes with anodized films formed in sulfuric acid (to produce 1- $\mu\text{m}$  thick layer of  $\text{Al}_2\text{O}_3$ ) and in battery electrolytes (to produce a duplex film with outer layer of  $\text{LiPF}_6$ ) will be prepared and coated with cathodes of  $\text{LiFePO}_4$  (Task 1). An electrochemical technique, which was proposed by Tobias and colleagues, will be evaluated as a tool for measuring small quantities of water (1-10 ppm) in battery electrolytes containing EC, DMC, and PC as solvent (Task 2). The electrochemical cell for *in situ* Raman spectroscopy of Al in battery electrolytes will be designed and constructed along with optics to direct laser light onto the Al sample and to collect Raman-scattered light from the Al sample (Task 3). Inspection of current collectors from life-tested coin cells will continue with an emphasis on cells that utilized new electrolytes (*e.g.*, salt of  $\text{LiBOB}$ ) (Task 1).

**STATUS SEPT. 30, 2004:** The contribution of corrosion of current collectors to battery overall capacity loss will be quantitatively expressed. The mechanism of passivation of Al and the identity of the passive film of Al will be determined in battery electrolytes that contain  $\text{LiBOB}$ . The possible role of particular cathodes in causing corrosion of Al current collectors in electrolytes with  $\text{LiPF}_6$  and  $\text{LiBOB}$  will be identified. The likelihood of corrosion of Al current collectors in  $\text{LiBOB}$  electrolytes will be compared to the susceptibility of Al current collectors to corrosion in  $\text{LiPF}_6$  electrolytes.

**RELEVANT USABC GOALS:** 10 year life; < 20% capacity fade.

**MILESTONES:** 1) Determine influence of water contamination on the resistance of cathode-coated Al to corrosion in battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$ . (8/05). 2) Determine relevance of Al's susceptibility to corrosion on battery capacity loss. (8/05)

## PROGRESS TOWARD MILESTONES

During the past quarter, work was focused on (1) inspecting aluminum current collectors in life-tested ATD batteries for evidence of corrosion, and (2) determining the details of the mechanism of corrosion of Al current collectors in Li-ion batteries.

We have initiated microscopic inspection of aluminum current collectors of 20 ATD batteries (with GEN2 electrolyte) that were previously charge/discharge tested different temperatures ranging from (approximately) 25-55°C. This work was undertaken to confirm results of earlier laboratory corrosion tests of aluminum and the results of microscopic inspection of life-tested Li-ion coin cells. Both the laboratory corrosion tests and the inspections of the coin cells' current collectors indicated aluminum current collectors were susceptible to crevice corrosion. The cathode-coated Al current collectors were removed from the ATD batteries by Azucena Sierra-VanDyke. Each cathode had one of two types of active materials:  $\text{LiFePO}_4$  or  $\text{LiCo}_x\text{O}_y$ . Initial results show extensive localized corrosion of the aluminum current collector even in ATD cells tested at room temperature (25°C) for a short period of time (less than 40 weeks). The results strongly suggest underdeposit corrosion (udc) of the aluminum current collectors. We are still in the process of examining the ATD batteries and will eventually perform a statistical analyses of the severity of corrosion once all of the ATD batteries have been examined. To assess the effect of temperature on the udc of aluminum, we plan to increment the temperature of laboratory udc tests from room temperature to 60°C.

Our earlier results had indicated that corrosion of Al current collectors occurred by a process called underdeposit corrosion, which is a type of crevice corrosion. Underdeposit corrosion of Al current collectors is probably the consequence of the microscopic porosity of the cathodes that cover the Al. While microporous cathodes act as crevice formers of Al, crevice formers such as a polyethylene disk and a black rubber with radially oriented grooves were found to not cause crevice corrosion of Al in Li-ion battery electrolytes. The failure of the polyethylene crevice to cause underdeposit corrosion of Al reproduced results obtained during the previous year. The inability of polyethylene and black rubber to act as a crevice former suggested that the battery's cathodes play an active role in the crevice corrosion of Al due to both the microporous structure of the cathodes and the cathode's electrochemical activity, *i.e.*, the micropores in the cathodes cause local changes in the composition of the electrolyte, which becomes corrosive to Al.

There are only few indications in the literature of catalytic oxidation of battery electrolytes on the cathode's surface at voltages operating during battery charging (*e.g.*, S.E. Sloop, J. B Kerr and K. Kinoshita, *J. Power Sources*, 119-121, 330-337, 2003), and there are no reports of the formation of corrosive oxidation products. Our study during FY 2005 showed that even high concentrations of water, which is a contaminant in the composite cathodes, do not lead to excessive corrosion of the Al, and from previous work of John Kerr et al., it seems that a plausible hypothesis for the direct role of the cathode in causing crevice corrosion of Al current collectors is related to the compositional changes resulting from the formation of relatively high concentrations of  $\text{PF}_5$  in the crevice solution. The  $\text{PF}_5$  results in attack of both the cathode and current collector.  $\text{PF}_5$  causes dissolution of the cathode by reacting with water contamination to form HF.  $\text{PF}_5$  locally corrodes the aluminum by acidifying the microscopic volumes of solution in contact with aluminum. We now plan to test the validity of the hypothesis that localized corrosion of aluminum current collectors is due to the generation  $\text{PF}_5$ . In particular, we will investigate the compositional changes of the crevice solution and examine the corrosion of aluminum in electrolytes of  $\text{PF}_5 + \text{EC}$  as a function of potential.

## **BATT TASK 6 MODELING**

### **TASK STATUS REPORT**

**PI, INSTITUTION:** J. Newman, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Modeling - Improved Electrochemical Models

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>  
High-voltage, high-power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIERS:** Poor transport properties, capacity and power fade

**OBJECTIVES:** Develop experimental methods for measuring transport and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

**APPROACH:** Use simulations to improve understanding of the SEI layer and particle volume expansion. Develop improved experimental methods for measuring transference numbers in liquid electrolytes.

**STATUS OCT. 1, 2004:** Modeling of dendrite growth is complete. A stability analysis that determines practical conditions under which dendrite growth can be inhibited or eliminated by mechanical means is complete. Comparison of SEI simulations with experimental results and refinement of the model is ongoing. Full characterization of transport in LiPF<sub>6</sub> electrolytes is ongoing.

**STATUS SEPT. 30, 2005:** Work will continue on a model for calculating stress distributions in electrode materials during intercalation. Full characterization of transport in LiPF<sub>6</sub> electrolytes will be ongoing. New projects may begin either on active material connected to a current collector and/or on including the Ni-MH system on the dualfoil model platform with side reactions.

**RELEVANT USABC GOALS:** 30 ohm-cm<sup>2</sup> area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit

**MILESTONE:** Model for calculating stress distributions in electrode materials during intercalation will be completed. (Dec. 2004)



## **PROGRESS TOWARD MILESTONES**

### **Stress Distribution in Electrode Material**

A model for calculating volume expansion and stress distributions in lithium-insertion materials has been used to estimate elastic stresses generated in carbonaceous and metal-oxide electrode materials during Li insertion and extraction. The model calculates the maximum stress in the particle as a function of charge rate, particle size, and Li diffusivity, using material, transport, and thermodynamic properties obtained from the literature. An auxiliary model for two-phase materials is used to calculate the stress generated during Jahn-Teller distortion in lithium manganese oxide. The stress calculations provide a means of predicting failure in Li-ion cells due to particle fragmentation and loss of active material contact.

### **Transport Property Measurement**

A new method is being developed in order to avoid the effects of side reactions in diffusion-coefficient measurements. Several anion-reversible electrode chemistries have been investigated including electroactive polymers and graphite. None of the chemistries investigated thus far exhibits a stable potential, eliminating them as possible candidates for use in Li-ion battery studies. A modeling effort has begun, investigating the effect of various parameters including particle size and porosity on the high-charge rate behavior of lithium titanate spinel.

## TASK STATUS REPORT

**PI, INSTITUTION:** V. Srinivasan and J. Newman, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Modeling - Modeling of BATT Program Baseline Chemistries

**SYSTEMS:**  $\text{LiFePO}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$

**BARRIERS:** Low power capability; capacity/power fade; poor low-temperature operation

**OBJECTIVES:** 1. Evaluate performance of the three baselines under HEV operation; identify the limiting mechanism in each chemistry. 2. Understand limitations of baselines when operating below room temperature. 3. Investigate degradation mechanisms and begin development of a cycle-life model.

**APPROACH:** Develop mathematical models for the BATT baselines. Perform experiments to complement models and extract unknown parameters. Optimize models to satisfy the EV and HEV goals, and use them to compare the baselines to each other. Perform experiments at lower temperatures and use model to understand the limiting processes. Incorporate life-limiting mechanisms into the models.

**STATUS OCT. 1, 2004:** Models for all three baselines have been completed and the performance limitations identified. A theoretical comparison of the three over a wide discharge range was ongoing.

**STATUS SEPT. 30, 2005:** Modeling of the baselines for HEV applications and optimization studies will be complete. Experimental measurement of kinetic and transport properties at lower temperatures (<RT) will be ongoing. Modeling of low-temperature operation will be ongoing.

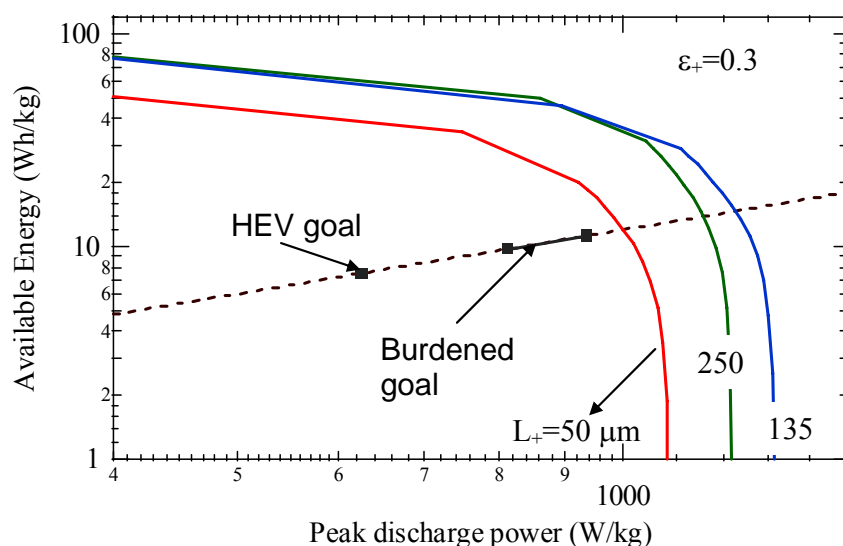
**RELEVANT USABC GOALS:**  $\text{ASI} = 30 \text{ } \Omega\text{-cm}^2$ , Cold cranking capability to  $-30^\circ\text{C}$ ; 300,000 shallow discharge cycles

**MILESTONES:**

1. Compare the three baselines under full discharge-time range. (Dec. 2004)
2. Identify the best baseline and the optimal design for HEV applications. (Aug. 2005)

## PROGRESS TOWARDS MILESTONES

We have been modeling the behavior of the BATT baseline chemistries in order to compare them on a common basis and evaluate their usefulness in EV and HEV applications. This study was conducted by finding the optimum design that maximizes the specific energy for a fixed time of discharge. While this was very useful, it was felt that the optimization should be extended to specifically address HEV operation. Therefore, taking the graphite/spinel cell as an example, we followed the FreedomCAR protocol to evaluate the available energy and the peak discharge power, as shown below. The figure shows the curves for three different electrode thicknesses along with the HEV goal, and the goal burdened by 30-50% to account for the weight of the device packing. The plot clearly shows an optimum thickness needed to maximize the power while maintaining the



same power to energy ratio (denoted by the dotted line). As the ratio of the anode to cathode is fixed, a thin positive electrode thickness means a relatively thin anode thickness. Electrodes that are too thin result in a significant polarization across the anode SEI. This polarization can be decreased if the electrode thickness is increased (resulting in a greater surface area for the current to transfer from the solid to the electrolyte phase). However, electrodes that are too thick result in an increase in the overall weight of the battery while not allowing for an increase in the power. The interplay between these two phenomenon results in an optimum.

The study detailed above clearly showed the impact of the anode SEI on the cell performance. It was determined that the anode used in this study (SL-20 natural graphite) was not a high-power anode. Therefore, we have decided to evaluate the use of the Mag10 anode which is used in the ATD Gen 2 cells. This anode has been shown to have a low ASI. We have collected experimental data on this system in a half-cell configuration. We are in the process of comparing the model to the data. Once this comparison is complete, the impact of this high-power anode will be evaluated.

## TASK STATUS REPORT

**PI, INSTITUTION:** A.M. Sastry, University of Michigan

**TASK TITLE - PROJECT:** Modeling – Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

**SYSTEMS:** Li/polymer and low-cost Li-ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the  $\text{LiFePO}_4$  cathode. Develop scale-bridging simulations that will allow identification of the best particle morphologies for both energy- and power-dense systems. Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

**APPROACH:** Using new simulations developed to model conductivity of the particle networks within both anodes and cathodes, we will expand our investigations with three major new thrusts: 1) development of scale-bridging models to determine likely electrochemical performance of cathode materials, taking direct account of the effects of particle shape and connectivity; 2) determination of the effect of mechanical compression on real batteries, accounting for both multiple layers and cell compression, and 3) extensive experimental and numerical simulation of conduction in new materials synthesized by other BATT workers (Striebel, Zaghib, Wheeler), and provision of guidance concerning the best morphologies to use.

**STATUS OCT. 1, 2004:** Experiments (LBNL and UM) and simulations on conduction and electrochemical performance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation, and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

**STATUS SEPT. 30, 2005:** Correlation of cathode performance with particle morphology, including fiber additives will be made. Completion of conductivity and mechanical experiments to quantify losses under realistic loads will be made.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, <20% capacity fade

### MILESTONES:

- 1) Provision of codes for numerical estimates of conductivity with a wide range of fibrous additives to other BATT workers. (Dec. 2004)
- 2) Development of full, finite element simulations of deformation of carbon additives under realistic loads will be completed. (Jan. 2005)
- 3) Implementation of algorithms to allow correlation of particle shape and size with electrochemical performance in Li-ion cells. (June 2005)
- 4) Experimental testing and numerical prediction of the effect of fibrous carbons on conductivity in  $\text{LiFePO}_4$  cathodes (with materials from Battaglia, Zaghib, Wheeler). (June 2005)

## PROGRESS TOWARD MILESTONES

- **Accomplishment toward milestone over last quarter**

Last quarter, we selected the commercial package FEMLAB© as a tool for simulation of Li-ion batteries, since it has the capability to perform the required multiphysics analyses. This quarter, we have begun to integrate our own algorithms of generating particle arrangements for active materials into FEMLAB. Ultimately, we aim to provide designers with a tool to visualize and test new electrode configurations.

At present, we are implementing models of published configurations of lithium-ion-insertion cells by Newman's group. At present, active materials are arranged in a regular fashion, *i.e.*, in face-centered cubic (FCC), or body-centered cubic (BCC) lattices, and the lithium foil/electrolyte/Li-ion-insertion-metal systems have been simulated. Our preliminary results suggest that electrode failure is likely to initiate near the interface of the electrode and current collector, due to stress induced causing by increased volume during lithium-ion intercalation. Next steps will include investigation of the effect of more random arrangements on battery performance.

- **Further plans to meet or exceed milestone**

We will continue developing mathematical tools for analysis of baseline materials, and plan to integrate with other DOE workers as validation of models, and in order to continue to provide guidance on selection/design of materials.

- **Reason for changes from original milestone: N/A**

## PROPOSALS UNDER REVIEW

<b>ORGANIZATION</b> <i>(Principal Investigator)</i>	<b>TITLE</b>	<b>STATUS</b>
Carnegie Mellon University <i>(P. Kumta)</i>	High capacity, reversible encapsulated porous nanocomposite anodes for lithium-ion batteries	Unsolicited Proposal-Under Review
Massachusetts Institute of Technology <i>(Y. Shao-Horn)</i>	TEM and AFM studies of nanoparticle coating on lithium battery materials: its effect on electrode stability, battery cycle life and battery safety	Unsolicited Proposal-Under Review
Graz University of Technology <i>(M. Winter)</i>	Investigations on safety and performance of intermetallic anodes of the BATT program in organic electrolytes by <i>on-line</i> mass spectrometry	Unsolicited Proposal-Under Review

## **BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) CALENDAR OF RECENT AND UPCOMING EVENTS**

### May 2005

- 15 - 20 207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)
- 22 - 27 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); email: [Josh.Thomas@mkem.uu.se](mailto:Josh.Thomas@mkem.uu.se); <http://www.icmcb.u-bordeaux.fr/libd>)

### June 2005

- 12 - 17 2nd International Conference on Polymer Batteries and Fuel Cells – Las Vegas, NV (Broddarp of Nevada, Inc. and The Electrochemical Society, 792-897-3027, [dbrodd@broddarp.com](mailto:dbrodd@broddarp.com)) Riviera Hotel and Casino
- 13 - 17 5th International Advanced Automotive Battery Conference (AABC-05) on VRLA for Traction Applications, and International Symposium on Large Lithium Battery Technology and Application (LLIBTA) – Honolulu HI (Menahem Anderman, Conf. Chair; <http://www.advancedautobat.com>) Sheraton Waikiki Beach Resort

### September 2005

- 25 - 30 56<sup>th</sup> Annual Meeting of the International Society of Electrochemistry – Busan, Korea (Contact: H Kim; [hasuckim@plaza.snu.ac.kr](mailto:hasuckim@plaza.snu.ac.kr))

### October 2005

- 16 - 21 208th Electrochemical Society Meeting – Los Angeles, CA (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)

### May 2006

- 7 - 12 209th Electrochemical Society Meeting – Denver, CO (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)
- 23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); email: [Josh.Thomas@mkem.uu.se](mailto:Josh.Thomas@mkem.uu.se); <http://www.icmcb.u-bordeaux.fr/libd>)

### October 2006

- 29 - Nov. 3 210th Electrochemical Society Meeting – Cancun, Mexico (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)